STUDIES IN THE CHEMISTRY OF PROTEINS AND POLYPEPTIDES: MECHANISM OF DYE SORPTION AND PHOTODEGRADATION ON WOOL AND NYLON.

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SUMMARY

Simple mono-azo dyes derived from m- and p-substituted aniline derivatives and ß-naphthol-3:6-disulphonic acid were applied to wool, silk and nylon and their fading rates studied under mercury arc or carbon arc illumination. In the latter case the samples were exposed in different conditions of acidity along with the B.S.I. standards, which were used as an actinometer in assessing the fading rates, averaged over a large number of experiments. In exposures to the mercury vapour lamp the time required to produce a just perceptible change was also noted. In both cases the values obtained were compared with those given by the unsubstituted dye and plotted against the 'σ' value (Hammett) in order to study the effect of the substituents on fading. For comparison the same set of dyes were then applied to different cellulosic materials and their fading rates again measured. Parallel thermal oxidation studies of the same dyes by hydrogen peroxide in aqueous solution were also made. On the basis of the results obtained it is tentatively suggested that dyes are reduced when irradiated on protein substrates, the substrate playing a specific part in the reaction, whereas they are photochemically oxidised on cellulosic materials which act only as inert substrates, on which the dye is dispersed in different physical states, the nature of which affects the fading rates.

Nylon in the above experiments behaved like cellulose, and in an opposite sense to wool or gelatin, in spite of its similarity of molecular structure in many respects.

The next section of the thesis describes work, designed to elucidate the nature of the reactions taking place in dyeing nylon and wool, which took the form of the application to these fibres of a number of organic compounds containing one or more simple groups, e.g., azo, hydroxy, amino groups, normally present in dye molecules, on dry wool or nylon from dry organic solvents. The results have revealed a number of interesting facts regarding the structure and bonding properties of these fibres, which are discussed in detail. It is found that only compounds capable of forming hydrogen bonds of OH.....O type are sorbed readily on these fibres and then only provided that their molecular size is such that they are capable of negotiating the pores of the fibre in the dry state. Compounds having an uninterrupted conjugated system of double bonds, e.g. benzene, azobenzene, were found to be sorbed apparently by van der Waals attraction. Nylon showed some differences compared with wool, which may be related to pore-size differences.

This work was followed by vapour phase sorption experiments of dry methanol on wool. The results are consistent with the view that hydrogen bonds are formed during sorption. In further experiments, dyed and deaminated wool and wool dried by various solvent methods showed effects apparently

due to blocking of the pores either by submicroscopic dye crystallites or by firmly held benzene.

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PREFACE

The suitability of almost any textile material for actual use, however strong and durable it may be, depends ultimately on its dyeing properties. An ideal material would absorb a dye readily so that it reached all of its constituent parts within a reasonable time and under practicable conditions of dyeing. Moreover it would retain the dye very strongly so that it could withstand washing, wear and tear, heat and light (sun). No doubt wool, Nature's greatest gift amongst fibres, successfully fulfils these requirements and no substitute is readily found. Thus an explanation of the reasons for its superiority remains a challenge to scientists, particularly to chemists.

The study of this particular fibre has led to important developments in the synthetic field. An explanation of the mechanism of dyeing of wool, however, remains a problem even though the technique of dyeing has made much progress, so that one can say without much exaggeration that wool can be dyed with ease to any practical requirement.

This thesis is an attempt to study the dyeing mechanism of wool by a two-way approach. It is as much important to understand the means by which any particular dye is held by wool as to measure its fastness in practical terms, and to understand the reasons for these. To study the former one needs a full understanding of the sorption forces of the material while to

study the latter involves a knowledge of the mechanism by which it loses the dye in various conditions of use.

The first section of the thesis deals with this last aspect with particular reference to light fading, while the rest of the thesis is devoted to sorption studies on wool (and nylon). Each section is summarised and discussed separately with the survey in brief, of the relevant literature.

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PART I.

INVESTIGATIONS UPON THE PHOTODEGRADATION OF DYES.

(The effects of substitution in azo dyes and the influence of the substrate upon fading).

SUMMARY

It is well known that certain vat dyes catalyse the formation of hydrogen peroxide when irradiated with visible light on cellulose. There is also some evidence that some proteins can form hydrogen-peroxide when irradiated with ultra-violet light. The possibility has therefore been examined that in light fading of azo dyes on protein fibres, hydrogen peroxide is first formed photochemically and then oxidises the dye in a thermal reaction. This hypothesis has been examined by studying the fading rates of a series of benzene-azo-R-acid dyes on wool, silk and nylon under various conditions of acidity, and comparing the results with those of thermal oxidation experiments using aqueous hydrogen peroxide. No evidence has been obtained that hydrogen peroxide plays any part in the fading reactions. It is shown that silk resembles wool in its effect upon the fading rate of the dyes examined while nylon shows quite independent characteristics. Finally comparison has been made of the same dyes on non-protein substrates and a possible mechanism of the fading of the dyes on proteins suggested.

INTRODUCTION

Light fading is one of the most troublesome faults to which coloured materials are subject and as such merits great attention of the textile chemists. Several dyes themselves have been subjected to numerous photochemical investigations under ideal and isolated conditions and quite valuable data is available in that field. However in their normal surroundings on the textile material various other considerations need to be taken into account e.g. the presence of moisture, air and impurities therein, the nature and intensity of illumination, the nature of the substrate, and the physical state of both the colouring matter and the substrate. It is with these considerations that most of the experiments here have been devised. It is well known that the light fastness of any given dye may vary considerably according to the fibre to which it is applied or that different dyes may show varied light fastness on the same material.

The Mechanism of Fading:-

(a) Oxidation:

A survey of literature shows evidence of oxidation products of the dye being formed in light fading on cellulosic substrates, e.g. Hibbert obtained isatin from faded indigo-dyed cotton, Haller and Zierisch obtained oxidation products from insoluble mono-azo dyes faded on cotton, and recently Couper identified

by chromatography a variety of oxidation products from 1:4-bis(methylamino)-anthraquinone on cellulose acetate. Mounier (presumably referring to cellulose substrates) observes that in the case of mono-azo dyes oxidising agents act as sensitisers, and reducing agents or the decomposition products formed by irradiation, act as restrainers. He also noted that the products of oxidation of azo dyes by hydrogen peroxide or other oxidising agents gave colour reactions with various reagents similar to those of azo dye fading products. It was pointed out by Desai and Giles that substituent groups e.g. nitro- and chloro-groups, which increase the resistance of oxidation of azo dyes, also appear to increase their light fastness on cellulose. Pinte and Millet at about the same time, Atherton and Seltzer, and later Atherton and Peters, also confirmed the beneficial effects of these groups on light fastness, and the adverse effects of the electropositive groups, e.g. methoxy and methyl groups. The experiments carried out by Harrison during 1911-14 in sunlight at low intensity and u.v. light on Methylene Blue (C.I.No.922) showed distinct oxidation effects; yet some of the dyes on cotton did not fade at all in evacuated or nitrogen filled glass tubes (Harrison; and also Gebhard; Lazarev).

Marney records (1950) that after accelerated weathering tests (exposure of wet patterns to arc-light), certain vat blue dyes changed shade in the direction of their oxidation products, the original shade being restored by a weak reducing agent.

(b) Reduction:

Oxidation of cellulose to oxycellulose in shortwave (quartz mercury-vapour lamp was found to be accelerated by the presence of certain dyes e.g. Benzo Violet, Diamine Sky Blue FF (C.I.No. 518) and Methylene Blue, even in vacuo (Harrison loc.cit) resulting in the reduction (fading) of the dyes. But Indigo (C.I.No.1177) and Crystal Violet (C.I.No.681) were not faded in this way. It was also found that the nitro-groups in aromatic compounds suffered reduction in u.v. light in the presence of cotton while the amino-groups were oxidised. Pure cellulose absorbs light strongly below 2000 Å (Kujirai) and obviously this absorption is responsible for the above reactions according to the Grotthus-Draper Law; hence in the normal sunlight where it shows weak or no absorption, it would be expected that some kind of oxidation rather than the reduction of the type described would be effective in fading mechanisms as in the case of Methylene Blue already mentioned in (a).

Mounier and Seyewitz and Mounier, found that certain nitrohydrocarbons were decolourised when irradiated on cotton, silk or wool, the reaction being sensitised by the reducing agents and inhibited by the oxidising ones. This was explained by them as being due to reduction (in the presence of cotton) to azoxy and hydroxyazo compounds which are subsequently oxidised to colourless products.

Atherton and Seltzer, in their work on the fading of amino-azo dyes on cellulose acetate, attributed the fading reaction to

oxidation. But Atherton and Peters noted that dyes containing one of the following groups, m-NO_2, p-NO_2, p-$COCH_3$, had anomalously low light fastness, which they attributed to these groups being reduced to give compounds of more fugitive character than the originals, as a first step in fading.

In light of wavelength 3400 Å some photolytic degradation of undyed cotton takes place in air or oxygen, (Egerton - 1947) which apparently may be due to either the impurities in cellulose which are capable of absorbing above 3400 Å and initiating the reaction; or due to the few active groups(CHO or CO) produced in the chain as a result of primary thermal oxidation, which then form the nuclei of absorption in the region to start the chain reaction affecting the entire molecule. This explanation has further been substantiated by work on synthetic polymers (Burgess). Thus it seems quite reasonable to assume that even a photochemically inactive dye will come in contact with reducing substances on cotton in normal sunlight (Harrison 1912, Whealan and Peat). However, these reducing agents do not seem to be powerful enough to attack the azo group itself (the available evidence is in favour of this being attacked by oxidation).

Similar observations in the case of non-cellulosic substrates particularly proteins are not many but it has been known for more than a century e.g. in photochemical reproduction of illustrations, that potassium dichromate when irradiated in gelatin insolubilises (tans) the latter by being reduced to

chromic salts.

Biltz and Eggert have shown that two molecules of gelatin react with one molecule of insoluble chromic-chromate to give a non-swelling adsorption complex; rather high quantum yield being involved compared with that encountered in the normal fading experiments.

(c) The nature of the fading agent and the possible mechanism.

Very little is known of the nature of the fading agent except for the generation of H_2O_2 by irradiation of certain dyes in air. Recently Blum and Spealman have noticed the formation of H_2O_2 on irradiation of aqueous solutions of Eosin (C.I. No.768) and Fluorescein (C.I.No.766) in air, which has not been identified otherwise as a fading agent - except in the special circumstances of photolytic sensitisation of cellulose. Hydrogen peroxide is also produced by irradiation (at 2536 Å) of aqueous solutions of a protein, serum albumen, in presence of oxygen (Roberts). The possibility that a similar reaction, catalysed by dye, might take place on protein fibres in visible light and so account for dye fading thereon has been examined in the present work, but as reported later, has been ruled out.

Acriflavine (C.I.No.790) dispersed on dry silica dust and irradiated in dry oxygen at low pressure is alleged (Egerton) to produce a metastable form of oxygen - formed by transfer of energy from excited dye to the oxygen of air - capable of oxidising leuco-Malachite Green, but produces no H_2O_2 (Kautsky)

et al). Other similar examples are of certain vat dyes which exert the tendering effect on cellulose in visible or near u.v. light in the presence of air and also catalyse the fading of accompanying dyes. (Egerton; Scholefield and Patel; Lamigen). Colourless pigments like zinc oxide or titanium dioxide which absorb near u.v. light also can act as photolytic sensitisers even though they may not be right in contact with the fibre itself. All these compounds, whether dyes or pigments are known to form H_2O_2 on irradiation in aqueous solutions or suspensions. Thus their tendering effect on fibres seems to be due to H_2O_2 or activated O_2 which may extend even to the closely situated undyed material (Egerton). Basic and sulphur dyes, and the thiazole direct dye Primuline (C.I.No.812) are also photolytic sensitisers for cellulose, but not the azo direct cotton dyes. Indeed, when an azo group is introduced into the molecule of an active thiazole dye, the activity is reduced. Insoluble azo dyes likewise appear to be rather inactive with the exception of one containing an anthraquinone nucleus (Ashton, Clibbens and Probert). More recently Ashton and Probert have made extensive tests of the tendering effects of some insoluble azo dyes on cotton, and noticed that these effects are of much lower order than the corresponding vat dyes already mentioned. There seems to be quite a close relationship, however, in either case, between extent of fading and tendering. Both these effects are promoted by increase in relative humidity, vat dyes having rather complex relationship

involving two factors independently related to the humidity factor. (Brownlie showed, in fact, that moisture is essential to the fading of direct dyes on cotton).

The general trend of all this discussion justifies the assumption of the formation of some form of active oxygen or a free radical derived from water or H_2O_2, as the basis of fading mechanisms. Hillson and Rideal's recent work has considerably added to this information. They conclude from their most novel experiments upon aqueous solutions of the dyes of azo and triphenylmethane types that a photo-excited dye molecule or radical must react with water molecules in the bulk of the solution to give an oxidised form of dye as a free radical, and hydrogen atoms.

$$\underline{D} \xrightarrow[h\nu]{} D^x; \qquad \underline{D}^x + HOH \longrightarrow \underline{D}OH + H-$$

The free radical is unstable and reacts with further molecules of water; thus in a typical azo dye oxidation, the azoxy form e.g. $\begin{matrix} Ph-N=N-Ph \\ \downarrow \\ O \end{matrix}$ is produced while in reduction a hydrazine form e.g. Ph-NH-NH-Ph is obtained. The triphenyl-methane dyes, however, are completely disrupted during oxidation, but form leuco bases in reduction. The formation of free radicals in the form of excited dye molecules, rather than hydrogen atoms or hydroxyl radicals was detected by the polymerisation of methylmethacrylate present in the dye solution, on illumination and to some extent even in the dark. The low quantum efficiency of normal fading (of the order of 10^{-6}) is attributed by

them to the removal of hydrogen atoms as HO_2 radicals ultimately forming H_2O_2, thus preventing the reversal of the main reaction. Both these processes in themselves are very slow.

These authors believe that the conditions on a textile fibre are very similar to those in aqueous solutions, since there is usually sufficient moisture adsorbed on the fibre to provide the hydroxyl radicals needed to react with the dye. Some hydroxyl radicals may even be supplied by the fibre molecules themselves, e.g., cellulose. If, however, a solvent e.g., isopropyl alcohol (Blaisdell) gives hydrogen atoms more readily than hydroxyl ~~ones~~ radicals, reduction may induce fading wherein oxygen would act as inhibitor, reoxidising the leuco base to the dye and forming peroxides with radicals from solvent molecules. Then the earlier experiments e.g. in vacuo or pure gases which indicated the need for oxygen for fading would seem to involve firmly bound water on the fibre.

The actual mechanism of breakdown of the azo group has, nevertheless, not yet been determined. Atherton and Seltzer, like Hillson and Rideal speculated on the initial formation of an azoxy compound; Desai and Giles on the other hand, suggested that the hydrazone form of the dye is attacked by hydrolysis to give a quinone and a diazo compound through the oxidation of a phenyl hydrazine derivative. Rowe and Dangerfield had suggested a similar hydrolytic mechanism to account for the breakdown of some azo-dyes in boiling water or acid, while Fierz-David et al believed the C=N link of the hydrazine form to be vulnerable.

The latter workers also suggested the rearrangement of the azo form to give a substituted aminoquinone, breaking down to the same products (e.g. hydroxyquinone and sulphanilic acid in this case from a sulphanilic acid ——→ ß-naphthol dye).

The recent determinations by Burawoy et al of the influence of substituent groups on the proportion of azo-hydrazone tautomers in unsulphonated benzeneazo-naphthalene dyes in certain solvents (including ethanol and water) show, however, that those groups which retard oxidative fading (e.g. NO_2) increase the proportion of hydrazone tautomer. If this also is true of the dyes in their solid state in the fibre, it would mean that the azo and not the hydrazone tautomer is the one most readily attacked. How far, in such circumstances, an o-hydroxyazo chelate ring would protect the azo group needs further study.

PRESENT WORK

We, in this laboratory, have carried out the following investigation, the part of which done by this author forms this section of his Thesis. The other work which was carried out simultaneously by his colleague Mr.N.Macaulay (NM) and which is reported in detail elsewhere has been summarised very briefly to keep the continuity and to bring the conclusions up to date.

Simple mono-azo dyes of both water-insoluble and water-soluble types derived from ß-naphthol, 2:3-hydroxynaphthoic acid anilide and ß-naphthol-3-6-disulphonic acid (R-acid) coupled with diazotised aniline and its m- and p-substituted derivatives, have been applied to a variety of substrates, both transparent and opaque, including cotton, wool, silk and nylon fabrics, films of cellulose ethers or gelatin, anodised aluminium strips, asbestos sheets, cellulose powder, filter papers etc., which have been illuminated by daylight, arclight or filtered and unfiltered mercury-vapour light. The rate of fading has been followed spectro-photometrically in transparent films, noting the time required for a given loss of dye; while in the case of the opaque substrates an indirect method of comparison has been used, based on the time taken to produce a just visible loss of shade. In the case of sunlight or arclight exposures, where the illumination is variable, the B.S.I. light fastness standards have been employed as a form of actionometer in

determining the relative fading rates by the method described later. It is interesting to note that these visual methods of comparison have proved to give results in close agreement with those obtained spectro-photometrically (see Appendix).

RESULTS AND DISCUSSION

The detailed fading data given in Tables 16 to 22 and the Appendix are presented as relationships between fading rate and '6' value of the substituent group in Figs. 4 to 13 and I to VII (Appendix). The difference between protein and non-protein substrates stands out clearly in that the effect of the substituents in the dye upon fastness is opposite in character.

The Nature of the Fading Reaction on Non-Protein Substrates:-

The explanation of the similarity in behaviour of these materials which seems to accord best with all the facts is that fading is an oxidation and that it does not involve any chemical reaction with this class of substrate. On the one hand, it seems unlikely that quite inert materials like porous clay, tile (Desai N.F.) or asbestos, or even methyl ethyl cellulose, can take part chemically in the fading. If this is so, then the substrate serves solely as an inert surface on which the dye is spread. Differences in the absolute fading rate of a given dye between substrates of this general class may then be ascribed solely to the porosity differences, which affect the degree of spreading of the dye on the internal surface and so influence the magnitude of the interface it exposes to air. The dyes used in this work have little or no affinity for the non-protein substrates, so that when the bulk of the solvent has evaporated they will separate as crystals or

as an amorphous layer. Even if some chemical bonding between the dye and the substrate operates in presence of solvent, this may be of no consequence as compared to the aggregation of the dye molecules on evaporation of the solvent. This part has been further borne out by using sulphonated and unsulphonated series of dyes from the same series on tile (Desai N.F.), the former showing greater fastness than the latter series, the reason being that the more dispersed dye would have less tendency to form aggregates.

The Nature of the Fading Reaction on Proteins:-

This class of substrates definitely appears to take part in the fading reaction. The following influences which might affect fastness are discussed.

(a) Water solubility of the dyes.

(b) Transfer of energy from the irradiated dye molecule to the protein, which in presence of air and moisture helps the formation of hydrogen peroxide. This hydrogen peroxide oxidises the dye in subsequent thermal oxidation.

(c) Specific bonding of the dye molecules to the proteins.

(d) Variation in the tautomeric ratio of the dyes.

(e) Chemical reduction of the dye induced by the protein.

(a) Effect of water solubility:

Kienle, Stearns and Van der Meulen used R-acid dyes on wool and in gelatin film, and Atherton and Seltzer, and Atherton and Peters used benzeneazo-α-naphthylamine dyes in cellulose acetate film, comparing the relative fading rates when various substituents were present in the benzene nucleus. If these are present in the m- or p-position to the azo group, quantitative comparison is possible by the use of the parameter known as the Hammett's ' 6 ' value appropriate to each group. In all the cases a linear relationship was found to hold between the ' 6 ' value of the substituent in a dye and its relative fading rate compared with the unsubstituted compound. In the system of Kienle et al (soluble dyes) a 'positive' relationship appeared i.e. fading rate decreased with increase in ' 6 ' value (increase in electron-attraction of the group), while in the work of Atherton et al this relationship was found to be reversed (insoluble dyes). The second type of relationship e.g. improvement in fastness by introduction of a nitro-group, was detected qualitatively in fading of some insoluble azo dyes on cellulose or in oil media, by Desai and Giles, who showed that the ease of fading on these substrates is qualitatively parallel with the ease of oxidation of the dyes studied.

The results presented here (Figs.8,9,11,12 and Tables I to V, Appendix) show the reverse effect to that observed above when water-soluble dyes (R-acid) are applied to cellulose etc. and then they resemble the water-insoluble class. The effect of

fading water-insoluble dyes on proteins has not been determined in great detail on account of the difficulty of applying such dyes to wool. However whatever experiments have been attempted have been tabulated in the experimental part. The data are difficult to interpret for reasons explained elsewhere yet one may say that roughly wool shows a behaviour typical of protein fibres when soluble R-acid dyes have been used. If as explained in the previous section aggregation of dyes is important in determining their fastness properties the extremely fugitive nature of the colour developed on wool or silk by coupling the diazotised bases with the fibres themselves might be related to the true molecular dispersion of the dye in this state. (In this case apparently the order of fading has reversed as seen from the Figs. 10,13 which naturally would affect the results of the β-naphthol dyes when developed on wool (Figs. 10,13) yet the general slope in the latter series of dyes except with those having positive '6' values is of the expected order. As to why the diazotised bases when coupled with wool show reverse tendency is rather difficult to explain on the merit of a few experiments reported here. However if the dye forming unit forms the part of the wool molecule e.g. by coupling with tyrosine residues in the side chain, as against the normal dye molecule combining with wool by way of acid-base combination, hydrogen bonding or van der Waals attraction, whether the dye forming unit would be subjected to similar influence as in the latter case is questionable.

Work on these lines is in progress in this laboratory at the moment c.f. (c). Thus it seems safe to conclude that at least the water solubility of the dyes does not have any connection with the division of the substrates in two classes. (The water-insoluble dyes have been padded on to paper and the results show the same general tendency of non-protein substrates) (Fig.9).

(b) Possible action of hydrogen peroxide:

The photochemical formation of hydrogen peroxide followed by thermal oxidation seems a quite plausible explanation as

(i) The rate of light fading on gelatin (NM) or wool of the series of R-acid dyes on the one hand, and the rate of oxidation by hydrogen peroxide under acid conditions on the other, are influenced in the same sense ('positively') by the nature of the substituent group in the dye (Figs. 1,2,3 and 4,5,7).

(ii) A soluble protein, serum albumen is reported to form hydrogen peroxide on irradiation (Roberts) at 2500 Å. In the presence of an excited dye molecule, longer wavelength radiation might produce a similar action in the case of protein fibres. It was found that the relative fading rates of the R-acid dyes are influenced 'negatively' by the substituents when oxidised by hydrogen peroxide in alkaline solution, (or in gelatin film under alkaline condition - NM). If thermal oxidation by peroxide is responsible for fading experiments on proteins, then in an alkaline medium relative fading rates should also be

influenced 'negatively' by the same substituents. This was not borne out by the experiments, rather it was found that there was no significant difference in the nature of fading rates whether the experiment was carried out in acid, alkaline or neutral medium.

The individual data are rather scattered, but there is no doubt that they lie about the same straight line and indeed the mean fastness values for each dye show a very good straight line (see Fig.7). The tests carried out in the presence of pyruvic acid, a reagent for the destruction of hydrogen peroxide (Hartree) showed no significant difference in the relative order of the fading even though the absolute fading rates were considerably increased (Table 17 and 23). Thus it seems quite apparent that hydrogen peroxide plays no part in the fading of the dyes on proteins.

(c) Influence of bonding to the substrates:

Besides the electrovalent forces of bonding the acid dyes to protein, there are recognised to be hydrogen bonding and van der Waals forces operative, and equally important (Vickerstaff) so far as amino, amide etc. groups in protein and other suitable groups like azo groups in the dyes are concerned. If the latter type of bonding in the dye were to account for the observed difference in the substrates, then the experiments of fading these dyes on Cellofas A film with nylon salt (66), adipic acid, ethylene diamine or n-butyl-propionamide fail to

give any such evidence for the order of the fading rates of the dyes is not changed (NM). However, incorporating l-tyrosine (about 0.25% of the weight of the Cellofas B 690 (I.C.I.) used) in preparing films, tends to give entirely different result than noted by NM e.g. the slope of the relative fading rate vs. '6' value curve is similar to that in wool. Considering the previous result c.f.(a) of wool with which diazotised bases have been coupled and the present one, it appears that tyrosine content of wool has a definite role to play in the reduction mechanism of the dye e.g. through oxidation to quinone form, which is not possible if chelation takes place with an azo group introduced in the ortho-position (in tyrosine). Thus, to a certain extent, similarity of silk and wool in the fading mechanism is understandable. More detailed work on these lines is in progress in this laboratory particularly with a view to forming uniform films from viscous material like Cellofas B used above.

(d) Effect of tautomeric ratio:

NM has studied the spectral absorption curves for the whole series of sulphonated dyes in water and the several transparent films. From these curves, in comparison with those given by Burawoy, Salem and Thompson, who studied the ratio of azo and phenylhydrazine tautomer, as judged by the relative heights of their absorption peaks, in a number of o-hydroxyazo compounds, it is clear that the tautomeric ratio plays little

or no part in the fading mechanism.

(e) Evidence of reduction:

(i) If irradiated gelatin can act as a reducing agent towards dichromates, we may suppose that it can do so towards dyes and it is found in the present work that gelatin (NM), silk and wool behave so similarly towards at least one series of azo dyes, it seems reasonable to assume that dyes are subjected to reduction process when exposed to light on protein substrates in general.

When exposure is made in the presence of pyruvic acid (Tables 17 and 23) there is significant increase in the fading rate of each of the dyes of soluble R-acid type but the relative order of fading is unchanged. This is what would exactly be expected if the fading mechanism is reduction. On the other hand exposures in the presence of hydrogen peroxide show a slight tendency to decrease the fading rate. Thus one feels justified to suggest, if not conclusively, that fading of dyes on protein substrates involves reduction.

(ii) Mechanism of reduction:

On the basis of the present series of experiments it is not possible to speculate on this subject. It is improbable that proteins would act as donors of hydrogen like the hydrocarbon solvents reported by Hillson and Rideal for, if so, nylon, which has about the same proportion of hydrocarbon to polar groups in its molecule, would be expected to behave in the

same manner, but it does not (Fig.6). Neither does methyl-ethyl cellulose, which has a high proportion of hydrocarbon groups (NM)(Table 23v). The ultraviolet absorption of gelatin and nylon only rises to high value well below 3650 Å, the lowest effective wavelength used in the fading tests, and at that wavelength the films of these two substances had nearly equally low absorption. Neither of these substrates is likely, therefore, to be directly photoghemically excited under the present conditions. Wool, on exposure to sunlight and air, is decomposed, the cystine linkages being hydrolysed, with formation of sulphydryl and aldehyde groups and hydrogen sulphide, which is eventually oxidised to sulphur dioxide and sulphuric acid (Race et al). This may account for the reduction of dyes on wool, yet it is reported that (Breare) many azo dyes on wool exert a protective effect towards degradation in arclight. Silk, on the other hand, has no cystine linkages and gelatin very few. All this leads one to believe the individual characteristics of each protein are important in the photochemical reduction of the dyes.

The Influence of Ortho-substituents and of Sulphonic Acid Groups

The beneficial effect of o-substitution reported by Peters and Atherton (for OCH_3) groups is corroborated in the case of Orange I and Orange II (OH group) dyes by Desai and Giles. Also a considerably increased effect of the ortho and para groups in the nitro compounds has been noticed by the

latter authors. In Table 16 it is found that o-chloro- or 2:4-dichloro-groups, reduce the fastness while all others e.g. o-NO_2, o-COOH seem to increase it. Thus the large chlorine atom does not seem to protect the azo group by steric hindrance, as Atherton and Peters have suggested in the case of the o-methoxy group, while it may be possible that the chelation between hydrogen of the methoxy and an azo nitrogen do so. In other cases noted above e.g. COOH, the latter type of chelation may be responsible for its contribution to fastness. A relationship between light fastness on wool and the position of the sulphonic acid groups in the naphthalene nucleus of benzeneazo naphthalene dyes has been noted by Boguslovsky and Sadov. However, their observations are difficult to interpret in any plausible way except that the position of these sulphonic acid groups may be contributing to the amorphous or crystalline nature of the dye particles formed on the fibre when the water is removed, and so influence the surface area exposed. In the present experiments (Table 16) it appears that similar reasons could explain their contribution to fastness of the corresponding dye whether in m- or p-position in the benzene nucleus.

Attempted Detection of the Fading Products:

In order to avoid the complications due to degradations of the fibrous material, it was thought that the anodised aluminium film may be more suitable to study the degradation products of the dye after fading. No product whatever except the unchanged

dye was extracted even though control experiments of film dyed and unfaded, gave the types of the compounds expected (Desai and Giles). The direct test of detecting hydrogen peroxide showed no trace of hydrogen peroxide on irradiation of dyed wool. It appears that reaction is too rapid and proceeds straight to gaseous products. This aspect should also form an interesting and very important subject for further work in the field of fading mechanism.

GENERAL CONCLUSIONS

From the present and other work the following generalisation can be made:-

(i) Substrates fall into two general classes (a) proteins (b) non-proteins, on which the effect of the substituents is opposite in nature.

(ii) Non-proteins probably do not take part chemically in the fading reaction which is mainly of the oxidation type wherein dye, water and probably oxygen are involved, though certain groups in the dye may be simultaneously reduced.

(iii) Proteins probably do take part in the fading reaction even though they may not do so in an identical manner.

(iv) A substituent group meta or para to the azo group has the same influence on the relative fading rate on water-soluble as well as water-insoluble dyes on any given substrate; yet absolute rate of fading may differ depending on the physical dispersion of the dye on the substrate.

(v) The initial attack in fading is on the azo group and probably involves transfer of energy from the excited dye molecule to a water molecule associated with that group.

EXPERIMENTAL

Preparation of Azo Dyes:

The azo compounds used were all prepared by the normal procedure from purified intermediates. The water-soluble dyes were salted out either by sodium chloride or sodium acetate and then recrystallised from water; their purity was determined by measurement of moisture content (dried to constant weight at 140°C.) and by titanous chloride analysis. Most of them show a fairly high degree of purity (Table 1). It is probable that the impurities were sodium chloride and firmly bound water. However it was found that sodium chloride in excess of any probable impurity had no effect on oxidation rates. At a later stage these dyes were purified by passage through cationic and anionic exchange resins in sequence followed by exact neutralisation of the free dye acid so formed, with sodium bicarbonate, their purity then being determined by the dichromate oxidation method (Arshid et al). This was found to be of the order of 98.5 to 100%. The water-insoluble compounds were purified by recrystallisation e.g. ß-naphthol dyes.

Anodised Aluminium:

Pure aluminium foil (0.002 in.) was anodised in 3% aqueous chromic anhydride "Analar" quality solution at 45°C. for 1 hour using an e.m.f. of 40-45v. and a current density of 10 amp.per sq.ft. It was then thoroughly rinsed in water. The film is

substantially pure alumina (Al_2O_3). Strips (5 x 5 cm.) were cut and dyed in 50 c.c.s of 0.02% dye solution at 60°C., then well rinsed and dried at 120°C., no 'sealing' aftertreatment being given.

Asbestos:

Smooth, white asbestos sheet (1.2 g., ca. 1 m.m. gauge) free of organic matter, was first rinsed in carbon tetrachloride, then in hot water, impregnated with a 0.01 molar solution of dye, pressed between filter paper and dried thus between plate glass sheet at 100°C. This left about 0.3% dye in the sheet.

Cellulose:

Three forms were used: bleached, mercerised cotton sateen, smooth chromatographic filter paper (Whatman) and cellulose powder (pure). The colouring was done in the same way as on asbestos. (When a different percentage of dye solution is used, mention is made in the respective Table.) (N.B. The experiments described here on films are more of a qualitative than a quantitative nature. The Spekker with appropriate filter has been used to estimate fading, while at a later stage NM carried out quantitative experiments using a Unicam spectrophotometer and found similar results.)

Gelatin:

14 c.c.s of a 6% aqueous solution of gelatin, of pure

'inert' photographic quality was mixed with 9 c.c. of 0.0005 M dye solution and poured on a 'subbed' photographic glass plate (4 x 4 in.) on a screw levelled platform. When the film had set, it was placed in a steady stream of air from a fan until dry. This procedure ensured the production of films having uniform optical density over their whole area.

Methylethyl Cellulose:

A 4% aqueous solution of Cellofas A (I.C.I.) was prepared in the cold by stirring continuously for 24 hrs., then centrifuged at 2,500 r.p.m. for 1 hr. in 4 x 250 c.c. containers to deposit fibrous material. The supernatant liquid was then used for film casting as per gelatin. The films, however, were dried over 4 x 100 w. tungsten lamps. Only the central portion of the castings were used as the edges showed inequalities and thickening effects.

Nylon:

Patterns of nylon knit fabric as well as satins (0.5 to 1 g.) wetted with calsolene oil were dyed from acetic acid bath (1:100 liquor ratio) at 80-90^{o} and the dye allowed to be exhausted as fully as possible. The patterns were thoroughly rinsed free of acid and then dried (NM used nylon films).

Silk:

1G. portions of boiled off silk fabric were dyed to near

exhaustion in 0.2% shades (adjusted, in each case, to give equimolar quantities from the purity data - the same as in the case of nylon) from 100 vol.baths containing 1% sulphuric acid, on the weight of the material, followed by rinsing and drying.

Wool:

1 g. patterns of scoured worsted flannel were dyed by the method used for silk.

Other materials used unsuccessfully in forming films were sodium carboxymethyl cellulose (Cellofas B of I.C.I.), solutions of which proved to be viscous; and polymethylmethacrylate (ammonium salt) and polyvinyl alcohol, both of which failed to give coherent films.

Mounting of Coloured Substances:

The patterns were stapled to a piece of card with a hinged black card flap covering one-half of the surface. Cellulose powder was packed into tiny 5 x 1 cm. sample bottles, half-portions of which were exposed to light. Some experiments were also done with packing the material into the rectangular apertures of thick cards sandwiched between thin glass plates. The films were treated as follows. Strips were cut from the centre of the plate, the film surface covered with a second equal sized glass strip and the ends bound together. The sizes of strip were suitable for direct insertion in the spectrophotometer or Spekker.

Insoluble Dyes on Wool and Gelatin:

Attempts to prepare samples of wool or gelatin satisfactorily coloured with insoluble azo dyes were not very successful. If coupling was carried out *in situ* in gelatin, the dye crystallised out irregularly on standing; whereas on wool (Everest and Walker) some coupling with the fibre substances itself occurred. Application to wool by impregnation with solutions in glacial acetic acid gave very irregular fading results. Their general trend, however, seems to be quite in agreement with other experiments. This irregularity seems to be due to the formation of bulky and non-uniform aggregates on the fibre. It was considered undesirable to use dispersing agents to give more even colouration because this would complicate the system.

Self Colouration of Wool and Silk:

A series of aniline derivatives with *o*-, *m*- and *p*-substituents (e.g. Table 1) were diazotised (the amount taken being of the same order as would give a 2% shade of the corresponding R-acid dye) in 2.5 c.c. conc. hydrochloric acid, 50 c.c. of water, 5 c.c. of sodium nitrite (10%) and then the diazotised solution was neutralised to Congo-Red paper by adding sodium acetate. The wetted samples were then introduced and stirred for 10-15 minutes and left overnight in the refrigerator for completion of the coupling. The patterns were then rinsed thoroughly with cold water and dried. Patterns which were

taken out and rinsed after about 20 min. showed very pale colouration.

Hydrogen-peroxide Oxidation Tests etc.:

In Solution

Portions (2 c.c.) of dye solution (2.21×10^{-4} M) were buffered (std. buffer tablets) and diluted to 20 c.c. after addition of 2 c.c. of 30% (w/v) hydrogen-peroxide (prepared from 98% 'high test' H_2O_2) and kept in a 25°C. thermostat in the dark, in ground glass (quickfit) or rubber stoppered test-tubes. Agitation was not employed, as it tended to make the results inconsistent. Either small quantities of the liquid were removed at regular intervals or the whole of the test-tube was removed from the bath according to convenience for optical density measurement in a photoelectric absorptiometer (Spekker).

The experiments were continued for 6 hrs. for alkaline and neutral solutions, and 40 hrs. for acid solutions in which oxidation rates were lower. Before measurement of the samples from the alkaline peroxide solutions, they were diluted with an equal volume of 0.05 N hydrochloric acid to prevent the formation of oxygen bubbles on the surface of the cell.

Tables 2 to 14 show the rates of change of optical density of the various solutions at three pH values, and in Figs.1 to 3 the rates of decomposition relative to the unsubstituted dye are shown plotted against the '6' value.

The change of sign of slope of the curves so obtained with

change in pH value is very marked.

Irradiation Tests for Comparison with Peroxide Oxidation:

The exposures of wool and silk, at different pH values and in pyruvic acid and hydrogen-peroxide vapours, were made by hanging the samples in corked test-tubes, at equal distances from the arc over 1-10% aqueous solutions of glacial acetic acid, water alone, ammonia (0.88 S.G.), hydrogen peroxide or pyruvic acid, the patterns having previously been steeped overnight in the respective solutions. All the fading experiments were run in triplicate at each trial and the relative positions of the tubes were frequently changed, in a random manner, during exposure. Personal errors in observation were reduced by requesting two other workers to keep an independent record of fading wherever possible.

(Gelatin films have been also subjected to similar tests by NM).

Illumination:

Most of the earlier experiments were made by enclosed carbon arclight - some by daylight. In later stages of the work (the author and NM), mercury vapour light alone was employed for reasons specified below.

Daylight:

Exposures were made through glass to skylight with a

southern aspect. Fading rates were determined by the B.S.I. standards.

Arclight:

A 250 v. D.C. carbon arc enclosed in pyrex glass was employed, patterns being exposed at 9 in. from the arc against the inner wall of a glass cylinder, with free upward circulation of air (air temp. ca 40°C)§§. Fading rates were determined by the B.S.I. standards. Frequent random changes of position of patterns and standards were made.

Mercury vapour light:

General Electric "Osira" lamps of both 250 w. and 400 w. capacity were used, run directly from the mains supply with appropriate choke. A constant voltage transformer was tested, but it was found to reduce the illumination by as much as 90% and hence was abandoned. Cylinders of sheet aluminium, 17 in. diam. x 15 in. high, centred on the lamps, with an internal annular shelf for the samples opposite the mid-point of the arc, were used, with free ventilation space. The air temperature around the patterns was ca. 40°C. with the 400 w. lamp while considerably lower with the other. The relative fading rates were found to be identical in arclight or mercury vapour light.

(In all such fading experiments the problem arises of correctly comparing the fading rates of dyes which have different spectral absorptions and are illuminated by light which is never uniform

§§ Air temp. change below 60°C. has little effect (Lead). The actual temp. of the samples would be considerably higher. No doubt changes in humidity have great effect on many dyes (Lead) but the R.H. of the atmosphere surrounding the patterns appeared to remain constant at ca 30% in the present test (arclight) as determined by air-hygrometer.

in energy distribution. The integral total energy method of Atherton and Seltzer and Atherton and Peters, fails to take into account the relative quantum efficiencies of the different regions of the spectrum; for it has been found that with some dyes the efficiency is very high in the near ultraviolet and falls rapidly to zero near the centre of the spectrum (Collins). Preliminary experiments on R-acid dyes seem to confirm that near ultraviolet radiation is most effective in fading. Moreover, the dyes compared are of the same chemical class and hue.)

Computation of Relative Fading Rates in Daylight and Arclight:

The use of the B.S.I. standards has enabled a simple method of computation of fading rates of related dyes in the variable light of sun or arc to be worked out. A sample is considered to have faded when a just perceptible loss of depth is evident to the eye[§§], and it is then graded by the S.D.C. standard, which under the same exposure, shows a similar loss. An approximate estimate of grading intermediate between individual standards, when necessary, was made (in arclight) by interpolation on a logarithmic scale by noting the time at which the fade appeared, compared with that required to fade the standards immediately above and below.

It is then assumed that the observed loss of depth represents in each case, to a first approximation, the destruction of the same fraction α of the total dye. The S.D.C. standards from 1 to 6 have been shown by Ricketts to be uniformly spaced, each one fading at twice the rate of that next above. (As far as possible we have confined our work to samples below 6.)

§§ Morton (1949) considers that the "fastness of a dyeing should be assessed at the smallest depth of fade which is commercially significant".

The proportion α of dye faded is thus destroyed in a time tf^{n-1} or $\frac{t}{f} \times f^n$ where t is the time required for Standard No.1 to fade, f the factor by which the standards are spaced, and n is the grade number or rating of the sample.

$$\text{Hence} \quad \alpha = K \times \frac{t}{f} \times f^n \quad \Big| \quad \text{where K and K' are constants}$$

$$\therefore \quad t = K' \alpha \, f/f^n \quad \Big|$$

Thus in a time t the proportion of the original dye destroyed is the measure of the fading reaction rate which is inversely proportional to the antilogarithm of the grade number, and independent of the spacing factor, provided the fading is judged throughout on the same basis. Hence if the grade numbers of a substituted dye and the corresponding unsubstituted one are respectively n and n_o, the ratio of their rates of destruction is $\underline{n_o - n}$. By plotting $\underline{n_o - n}$ against '6' value for a related series of dyes, the effect of substituents upon fading rate can thus be determined. Figs. 4 to 13 show the result of this treatment of a number of light exposure tests. Data from single samples are scattered, but the observation of several replicates of each sample leads to a much improved linear relationship showing a definite influence of structure upon fastness, a result which demonstrates that the errors in assessment are random and not systematic.

When the results of the assessment plotted in this way on either non-protein or protein substrates (Figs. 4 to 13) are

compared with corresponding plots of fading rate data obtained by the more precise method of spectrophotometry (Figs. VI and VII, Appendix by NM), good agreement is noted between the slope and direction of the curves. This agreement therefore serves to justify the underlying assumption on which visual assessments were made. Some results, obtained by this method from manufacturer's data on the fastness of arylides of 2:3-hydroxynaphthoic acid (Brenthols) (Desai, Thesis, Ph.D., 1951) are also in the same sense as those obtained here.

Gradings in arclight were converted to the corresponding grading in daylight, before plotting, by use of the regression line of sunlight assessment on fadeometer assessment given by Morton. The fading data, in general, are no doubt only approximate, and the figures to the right of the decimal points are not considered individually very significant, though it should be pointed out they were each obtained by averaging several assessments. However the mean-assessment figures are quite significant even though the differences are smaller, because they are the averages of large number of assessments in different series of experiments.

In Mercury-vapour Light:

For opaque substrates the time of exposure required to produce just perceptible loss of depth was noted for each sample and the log. of the reciprocal of this value was plotted against 'σ' value for the corresponding substituent in the

dye (Figs. 10,12,13 and Appendix I to VII).

Fading in the transparent film which is only of qualitative nature here was determined by Spekker spectrophotometer in the usual way. At least 3/4 readings of optical density were taken at different places on the same film and then averaged. (Later NM used the Unicam SP 500 when it was acquired for the Department).

Throughout all the above fading experiments dyes were always exposed in complete sets i.e. sets containing the examples of each substituent group at a time in duplicates or triplicates and then the whole series was repeated. The B.S.I. standards were also used in duplicates or triplicates randomly distributed amongst the dyed samples under test.

Note on '6' Values:

Some '6' values may vary according to the type of compound containing the substituent. Thus, Hammett quotes two values for the pNO_2 group, one (+1.27) for derivatives of aniline and phenol and the other (+0.778) for the reactions of all other compounds. The first value has been used in the present case.

Direct Test for H_2O_2:

Ashton et al (Symp.S.D.C. 1949) have recommended the method of starch-iodide paper or bleached cotton for the direct testing of the H_2O_2 produced during fading of the dyed cotton. The method was repeated for wool, dyed and undyed and undyed cotton

in arclight exposures and mercury vapour light exposures without any relevant results for the reagent paper or cotton itself liberated iodine when thus exposed. The samples usually were exposed sandwiched between two glass plates.

However, by drying the freshly made starch iodide paper or cotton in an oven, conditioning to room temperature and then exposing to daylight, no colouring of the reagent was detected either in the case of dyed or of undyed wool.

Some Unsuccessful Attempts in Colouring Wool with Insoluble Dyes.

0.5% dye on the weight of the fibre was dissolved in cellosolve and poured in hot water kept well stirred mechanically, the fabric being present. A porous tower of aluminium was used to surround the stirrer so that fabric would not get entangled with the stirrer. Various liquor ratios (water:fabric) were tried (e.g. 1:50 to 1:1000)

Use was made of some dispersing agents in small quantities to achieve evenness without any successful results. Variation of temperature was also tried unsuccessfully, e.g. 50°C. to 90°C.

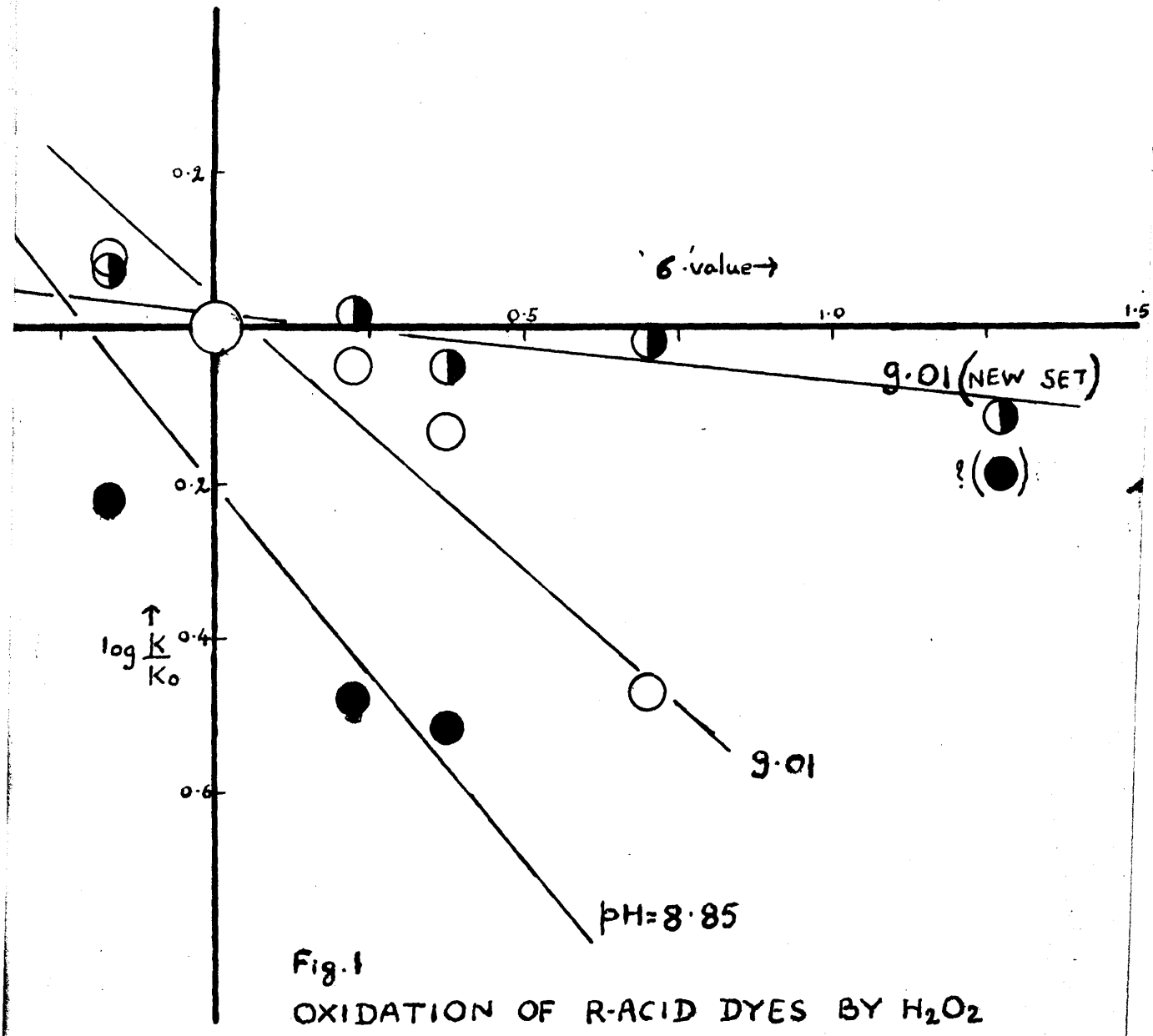
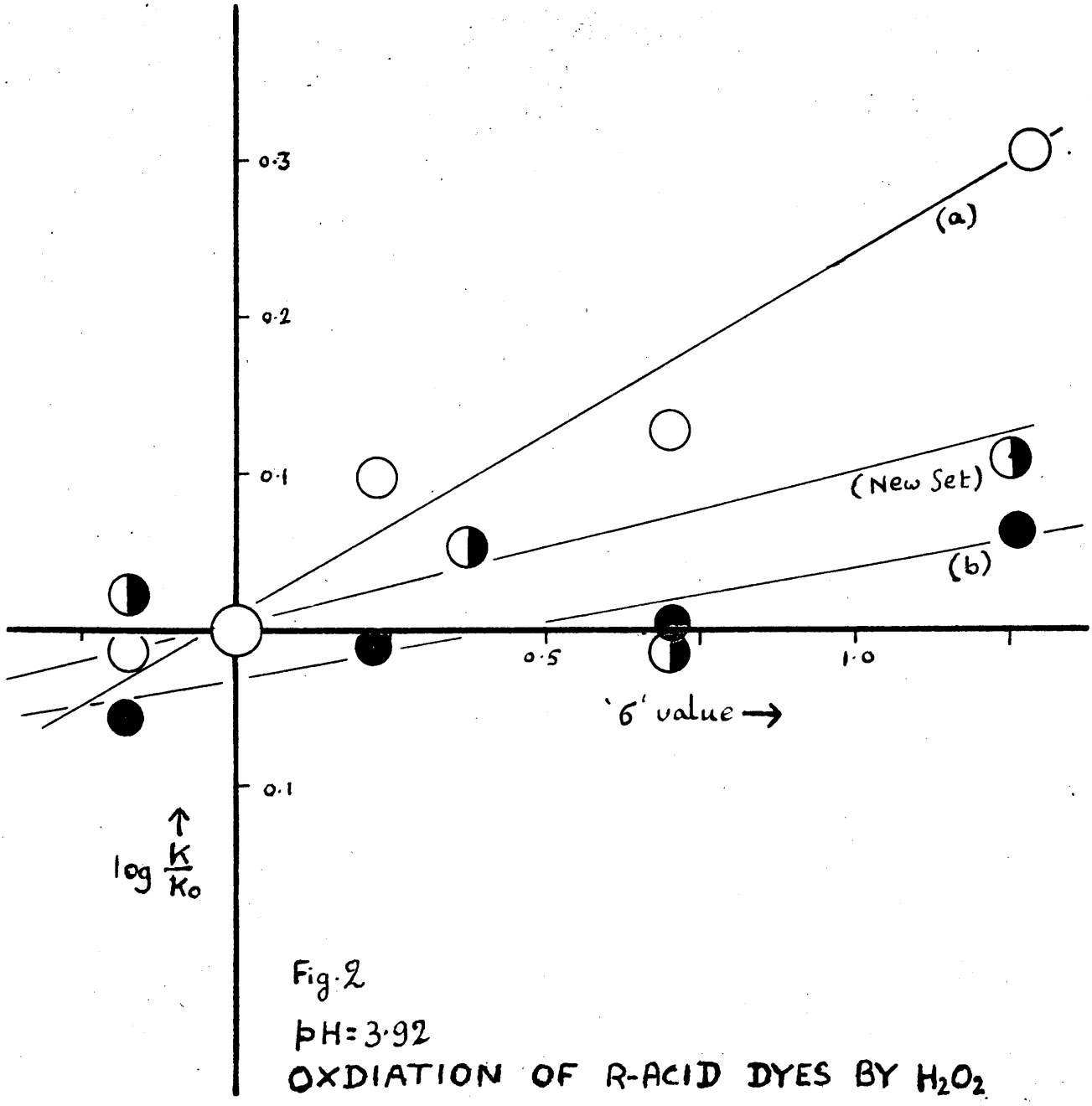


Fig. 1

OXIDATION OF R-ACID DYES BY H_2O_2



Fig·2

pH=3·92

OXDIATION OF R-ACID DYES BY H_2O_2

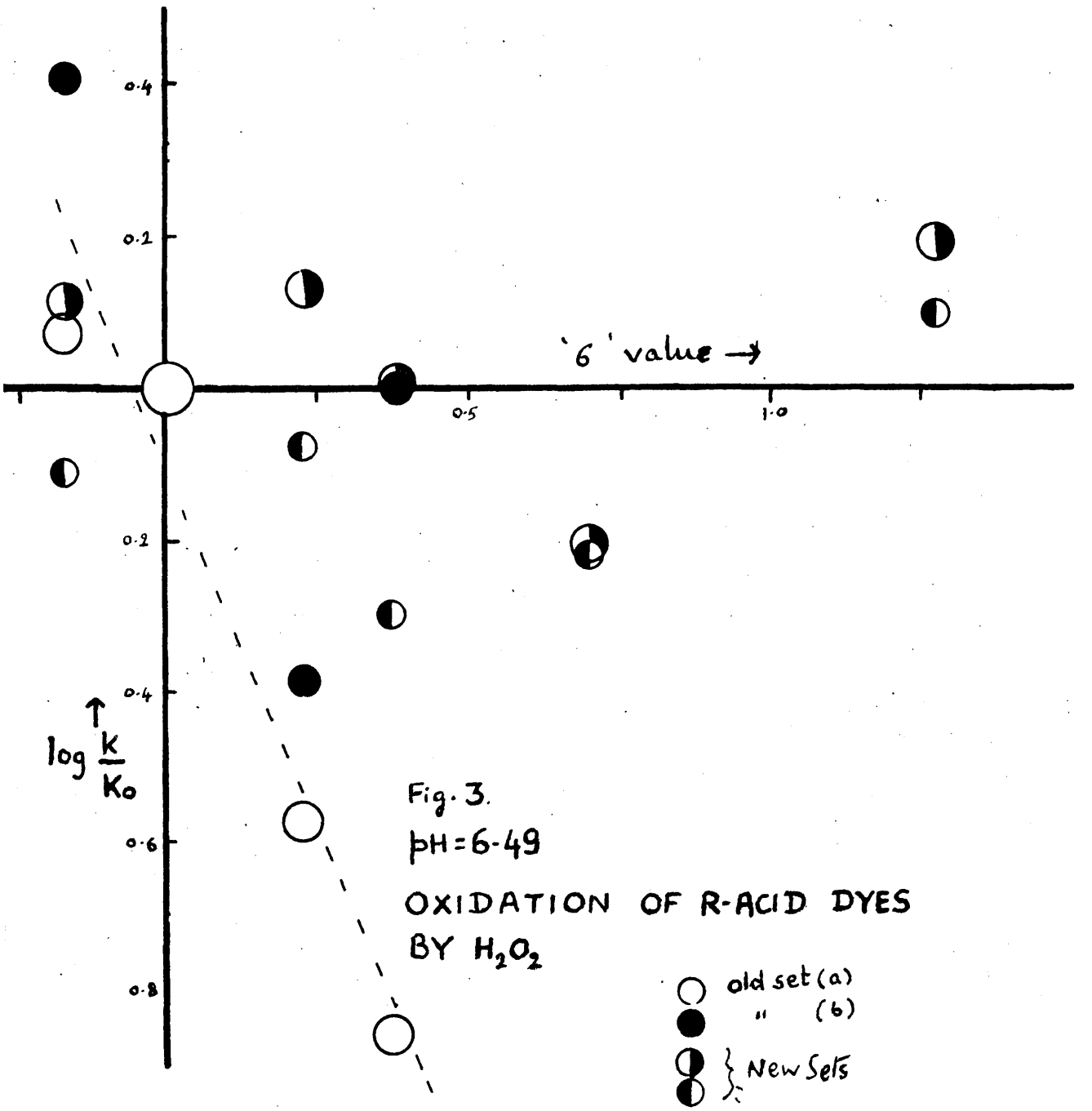


Fig. 3.

pH = 6-49

OXIDATION OF R-ACID DYES BY H_2O_2

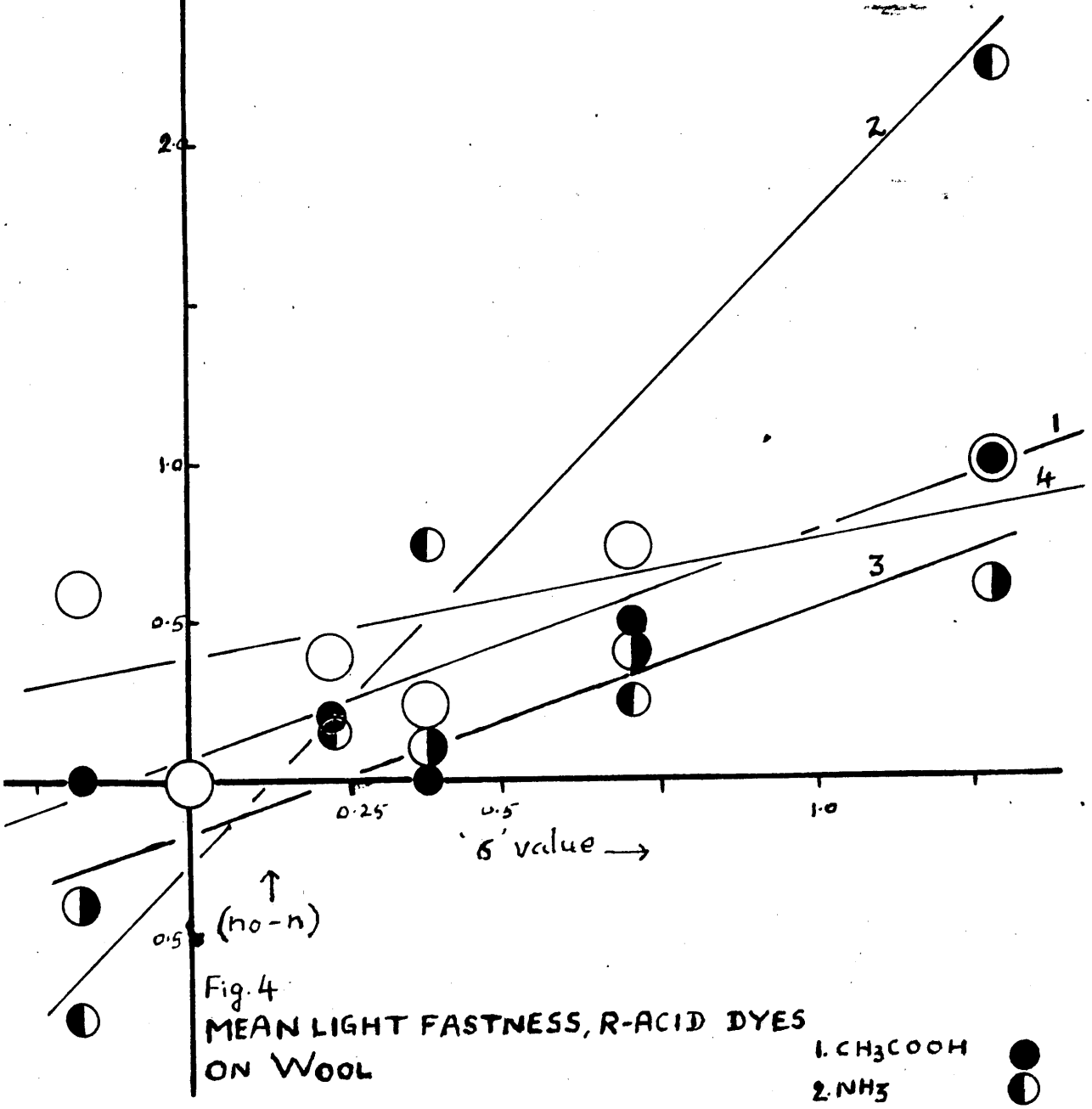


Fig. 4
MEAN LIGHT FASTNESS, R-ACID DYES ON WOOL

1. CH_3COOH
2. NH_3
3. H_2O_2
4. H_2O

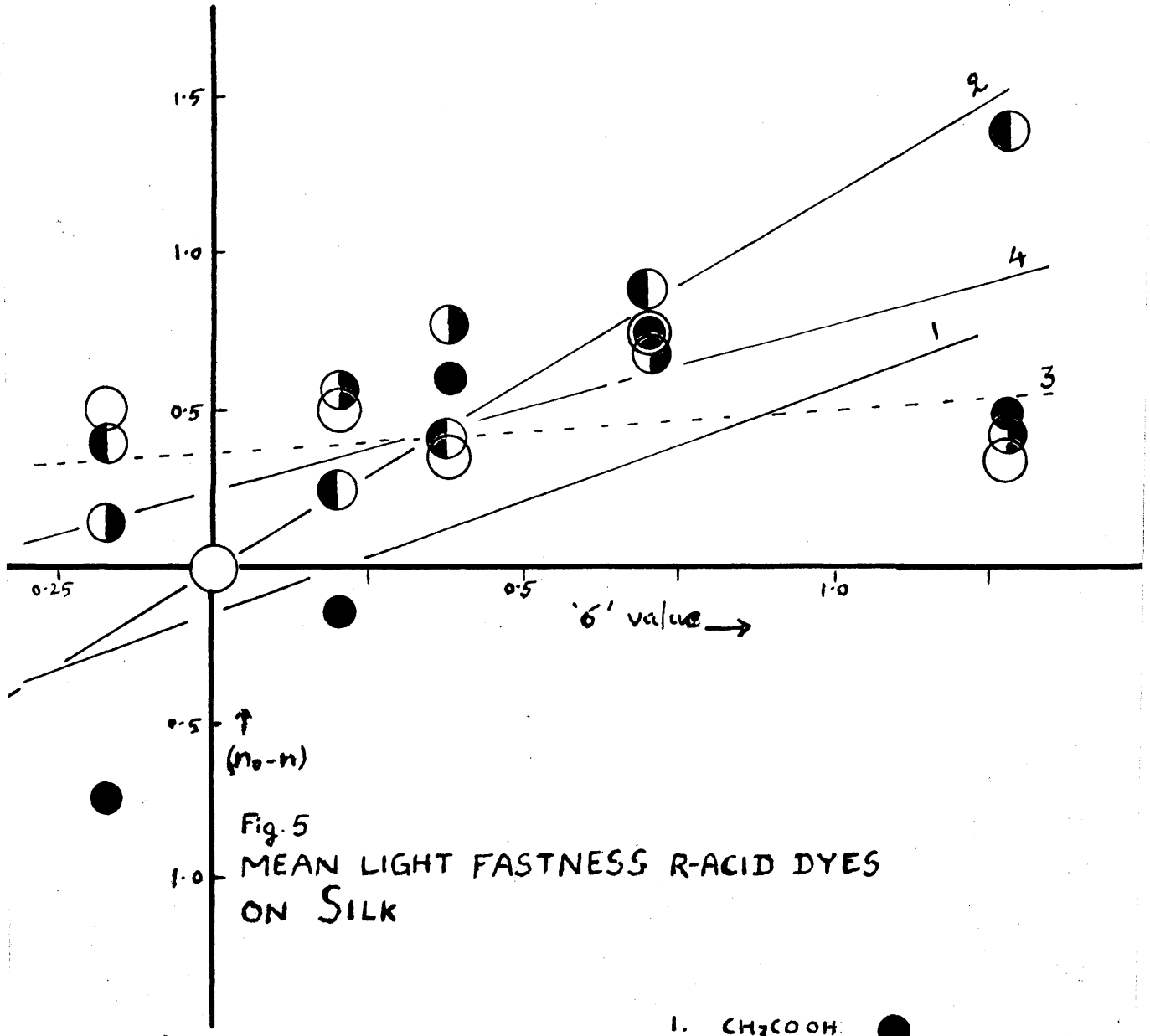
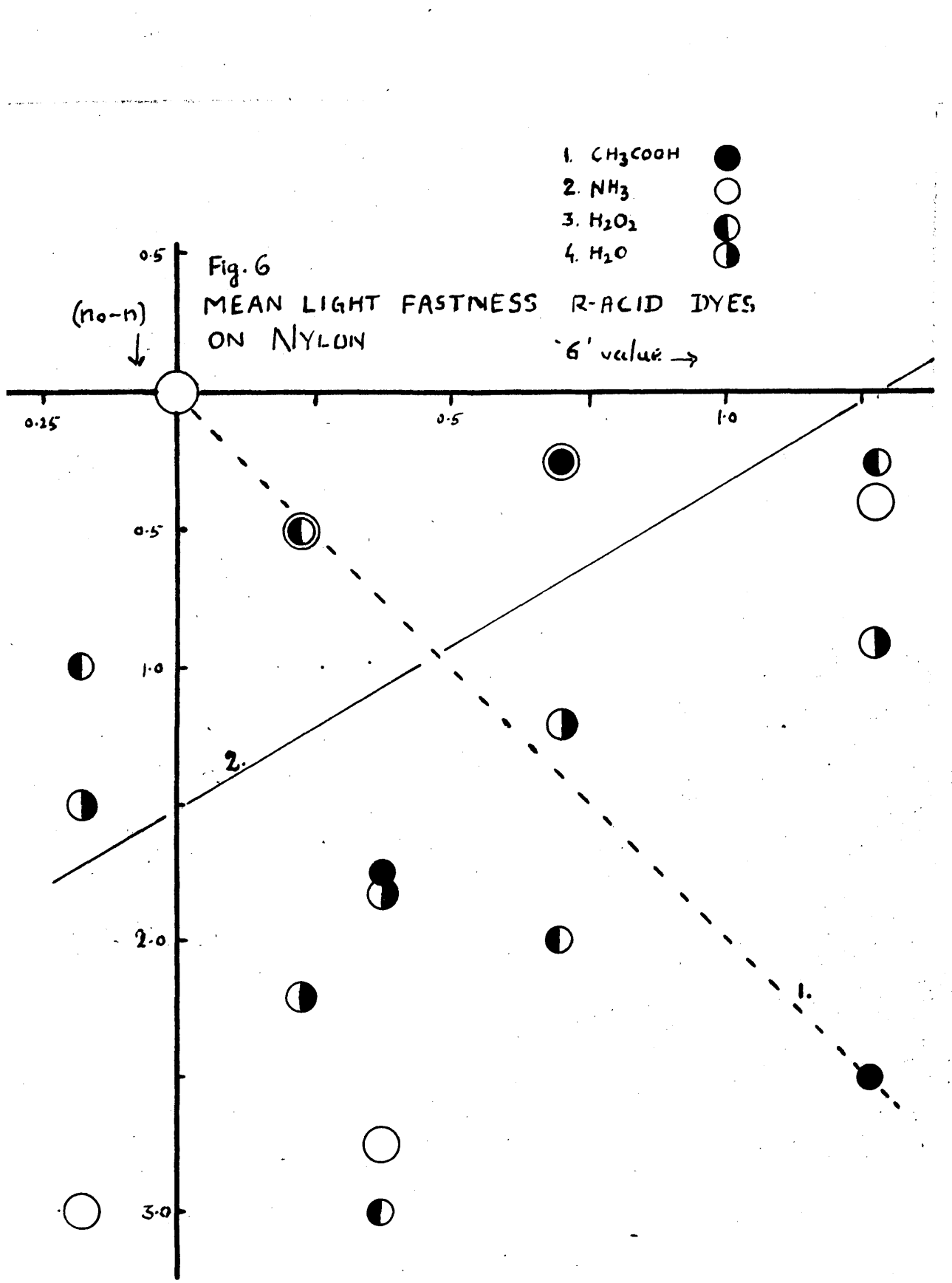


Fig. 5
MEAN LIGHT FASTNESS R-ACID DYES ON SILK

1. CH_3COOH
2. NH_3
3. H_2O_2
4. H_2O


1. CH_3COOH
2. NH_3
3. H_2O_2
4. H_2O
Fig. 6
MEAN LIGHT FASTNESS R-ACID DYES ON NYLON
(n_0-n)
'6' value →
0·5
0·25
0·5
1·0
0·5
1·0
2·0
3·0
1.
2.

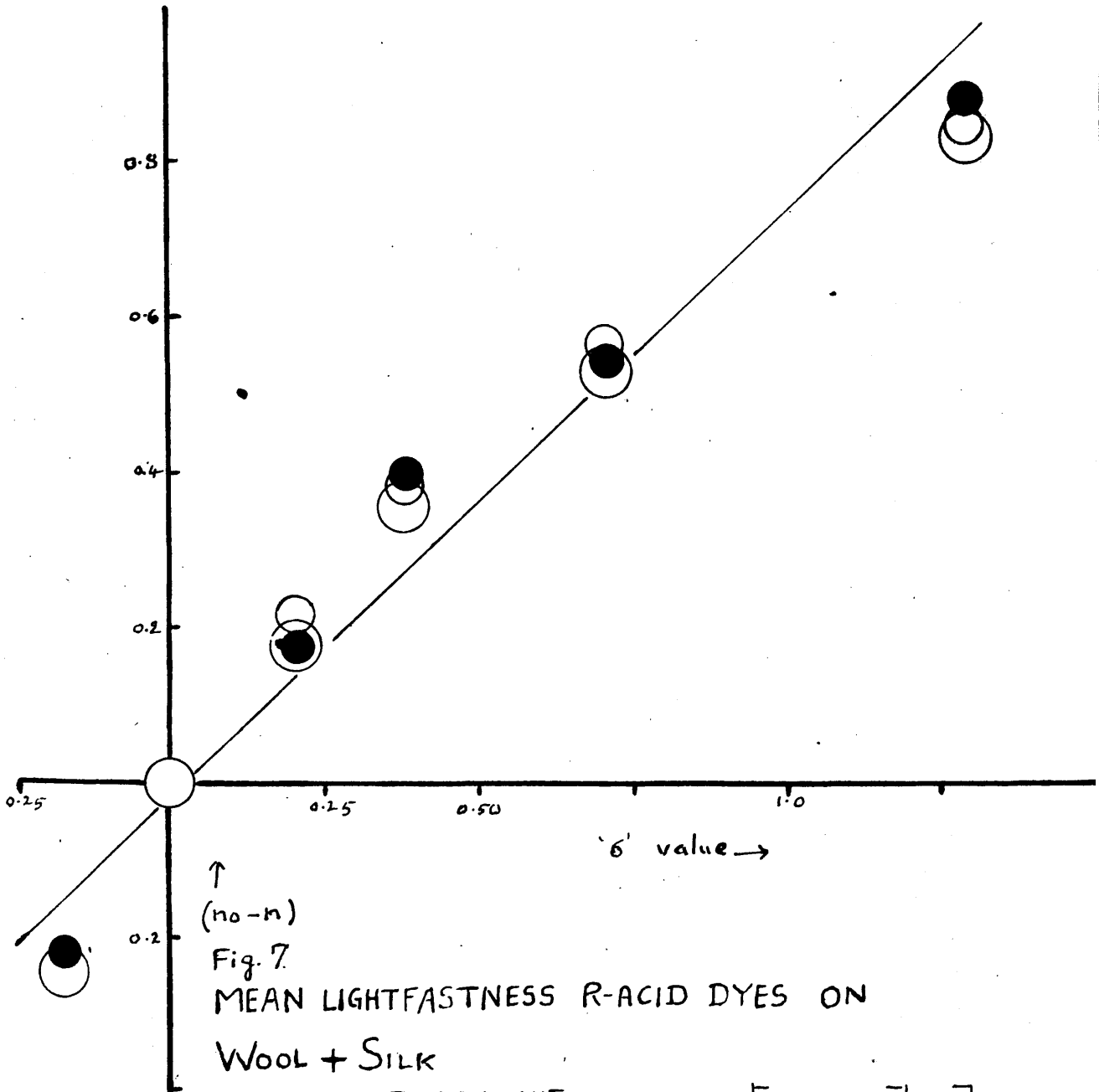


Fig. 7

MEAN LIGHTFASTNESS R-ACID DYES ON WOOL + SILK

CORRECTED TO DAYLIGHT

MEAN ○ [CH_3COOH + NH_3 + H_2O + H_2O_2 + PYRUVIC ACID] ● ○

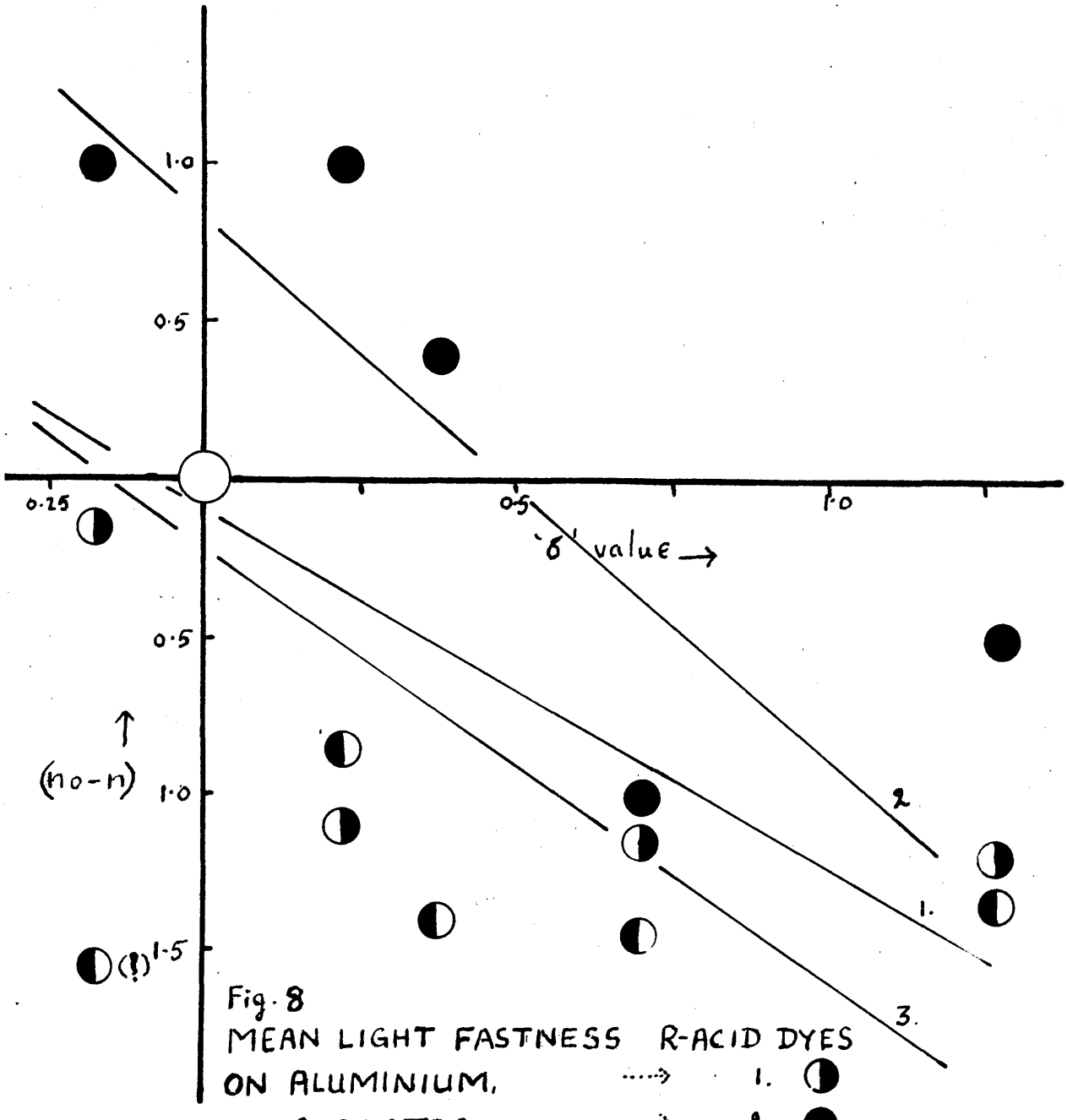


Fig. 8
MEAN LIGHT FASTNESS R-ACID DYES
ON ALUMINIUM, ····→ 1.
ASBESTOS ····→ 2.
CELLULOSE POWDER ···→ 3.

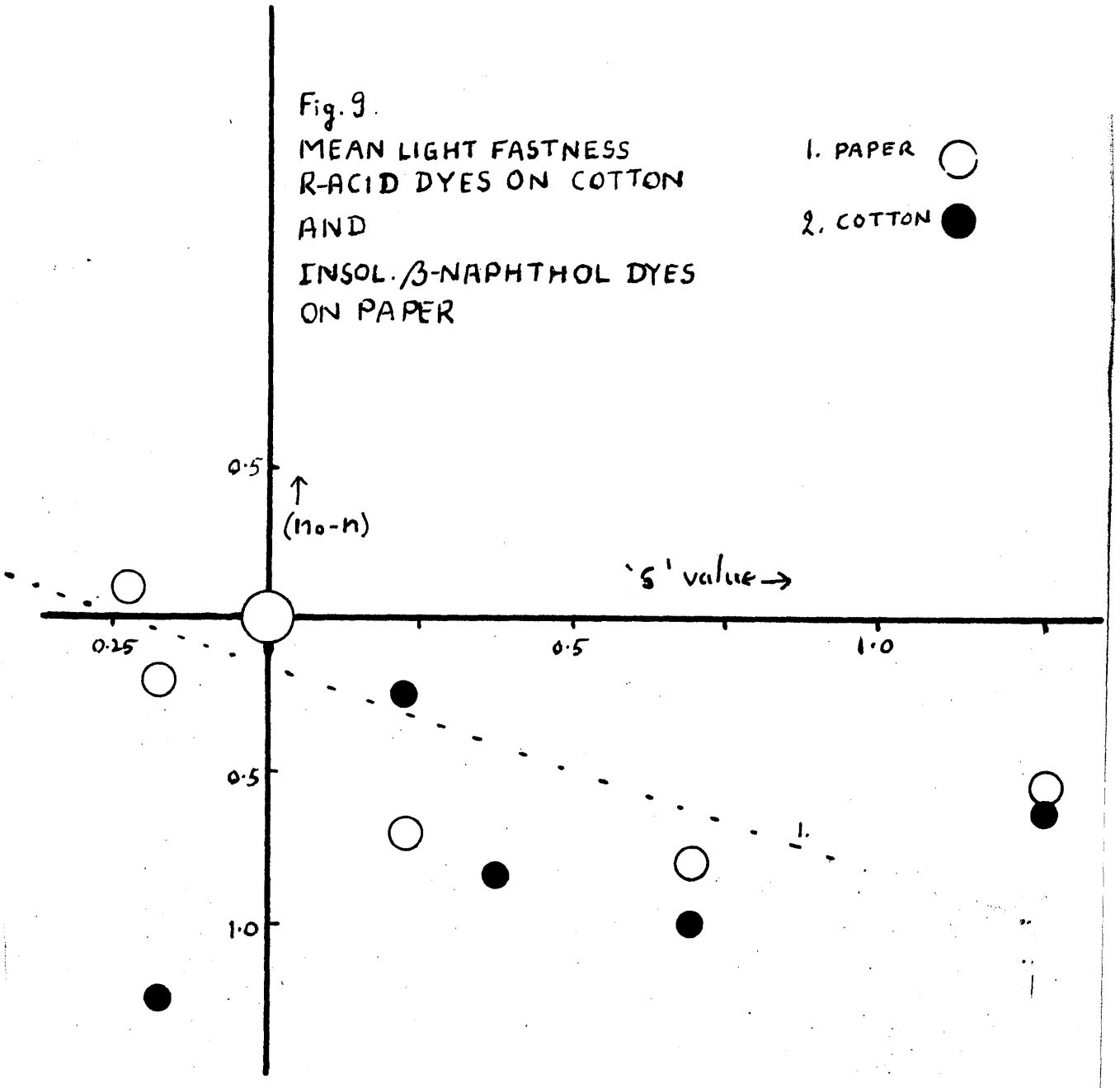


Fig. 9.
MEAN LIGHT FASTNESS
R-ACID DYES ON COTTON
AND
INSOL. β-NAPHTHOL DYES
ON PAPER
1. PAPER
2. COTTON
0·5
(n₀-n)
'S' value →
0·25
0·5
1·0
0·5
1·0

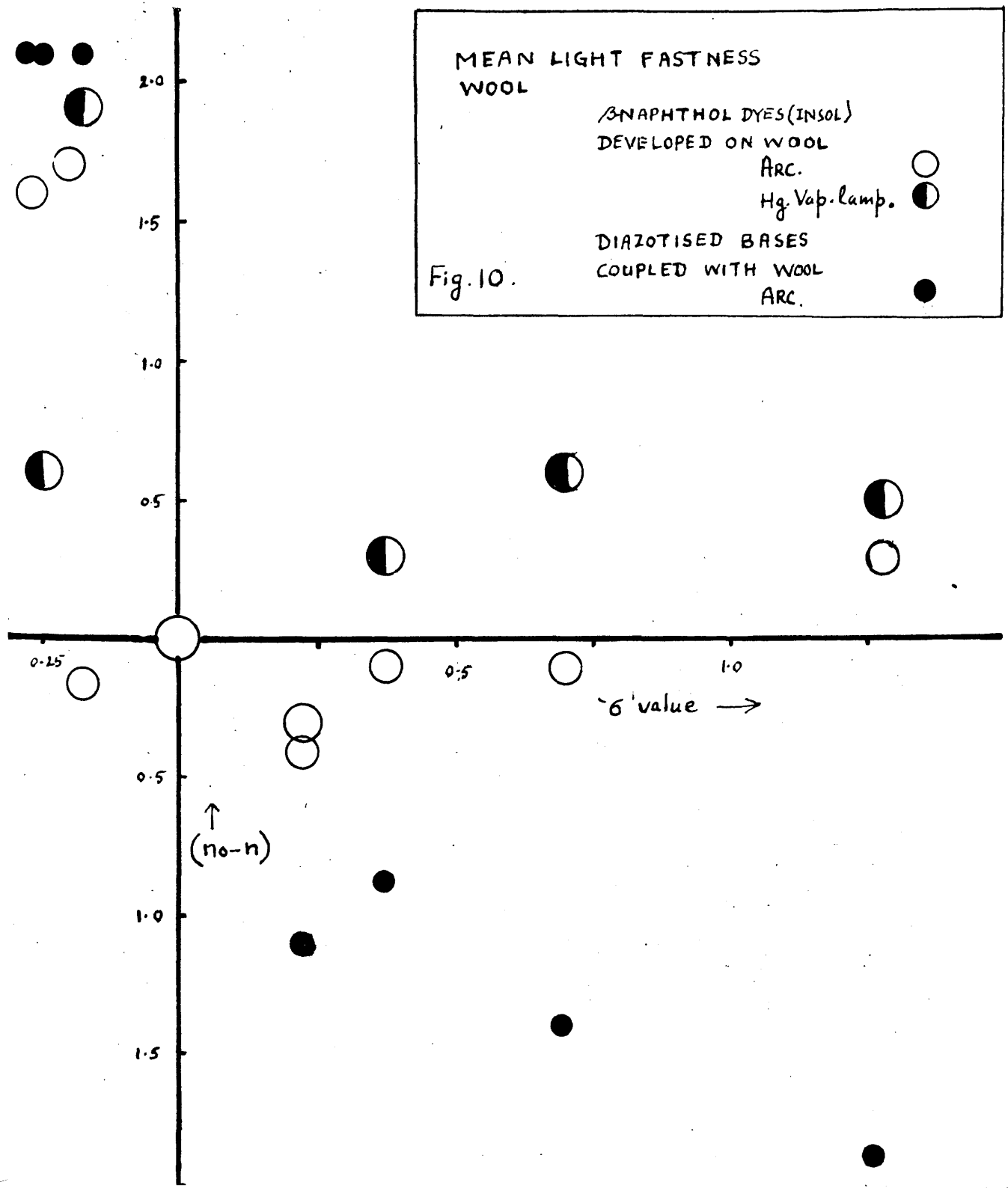

MEAN LIGHT FASTNESS
WOOL
βNAPHTHOL DYES (INSOL)
DEVELOPED ON WOOL
ARC.
Hg. Vap. lamp.
DIAZOTISED BASES
COUPLED WITH WOOL
ARC.
2·0
1·5
1·0
0·5
0·25
0·5
1·0
'σ' value →
0·5
(no-n)
1·0
1·5

Fig. 10.

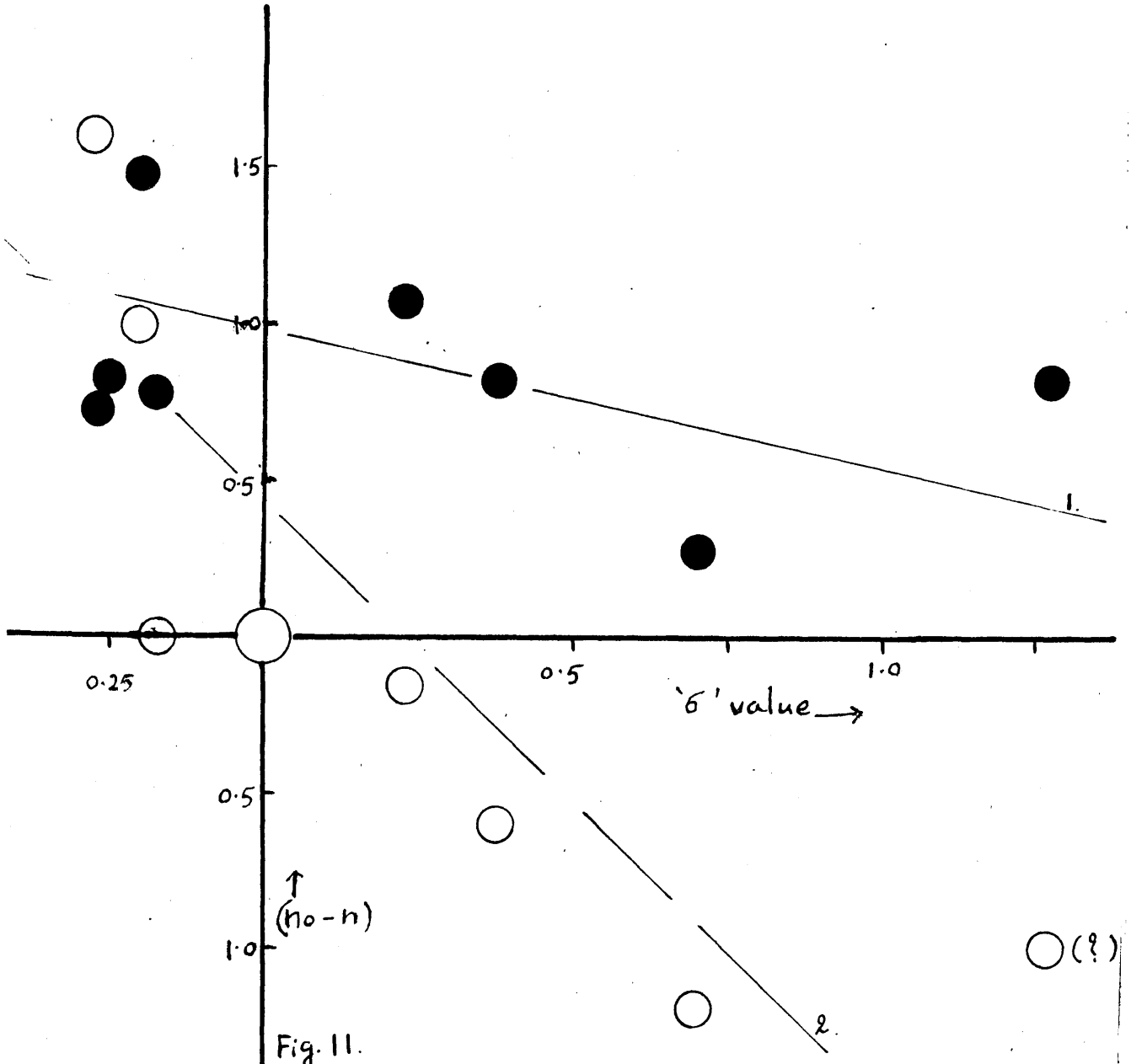


Fig. 11.
MEAN LIGHT FASTNESS R-ACID DYES ON PAPER AND ALUMINIUM
Hg-vap. lamp.

1. PAPER —: ●
2. AL. —: ○

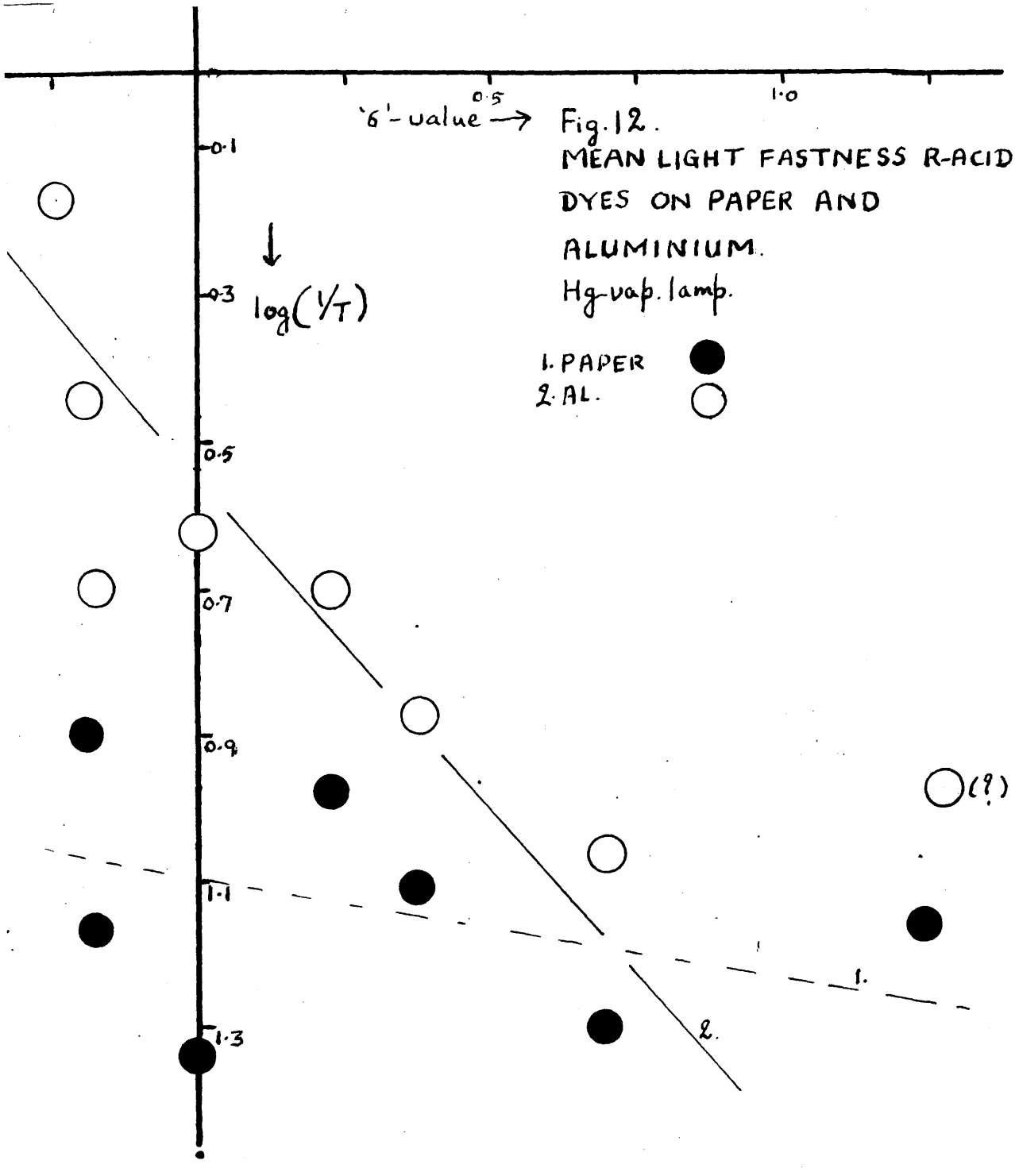
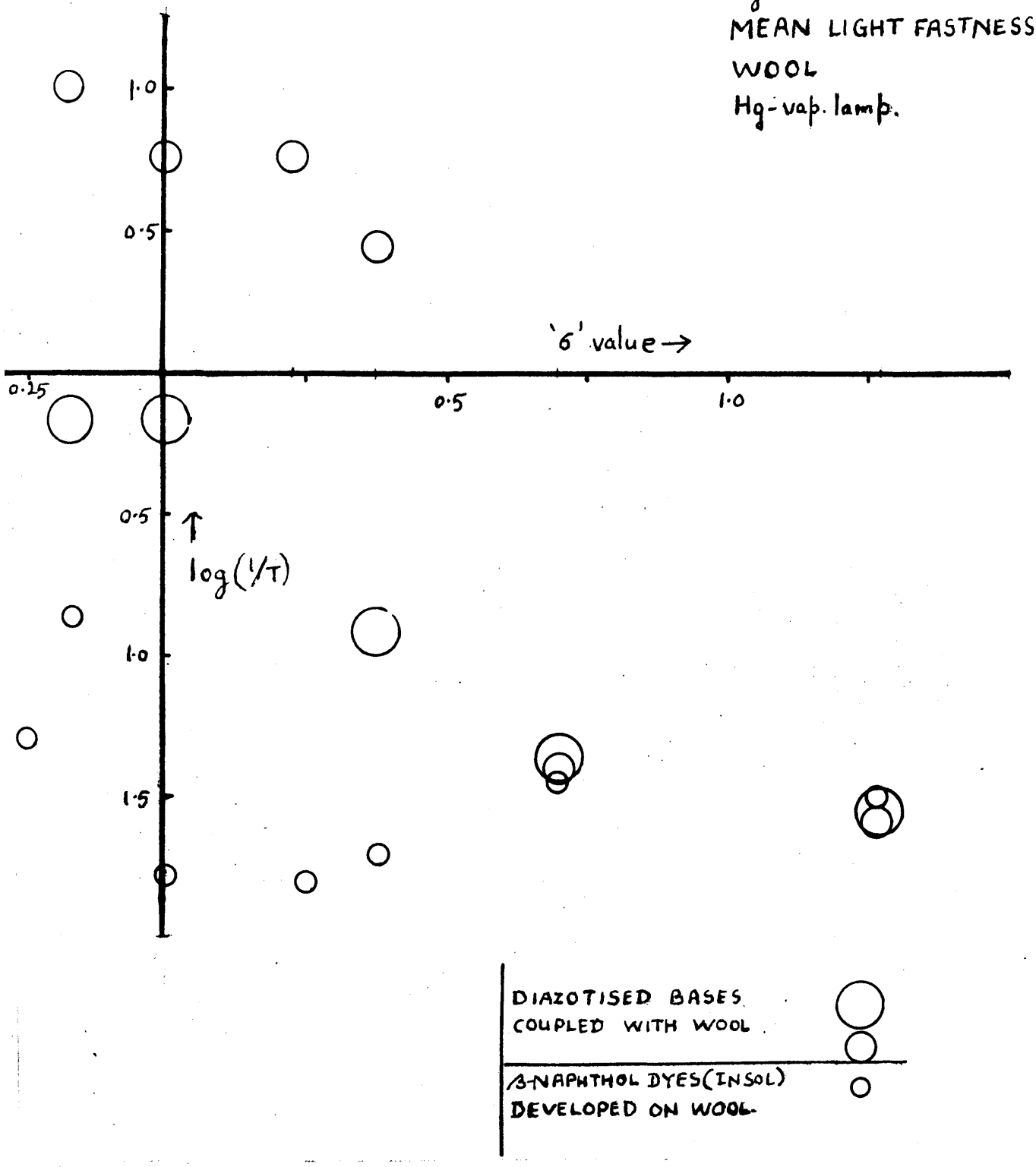


Fig. 12.
MEAN LIGHT FASTNESS R-ACID DYES ON PAPER AND ALUMINIUM.
Hg-vap. lamp.

1. PAPER
2. AL.

Fig. 13
MEAN LIGHT FASTNESS.
WOOL
Hg-vap. lamp.



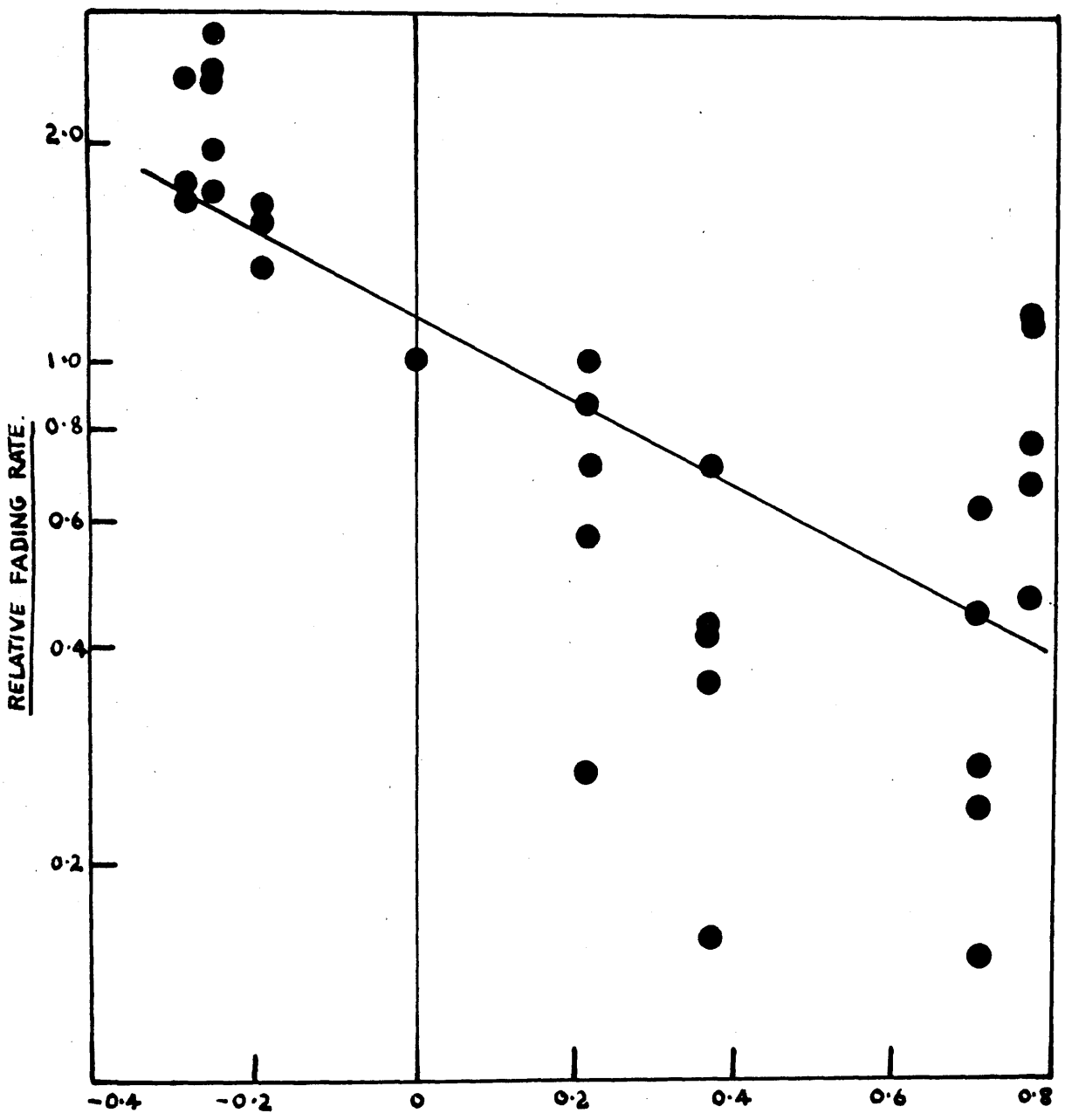


Fig. I
RELATION BETWEEN RELATIVE FADING RATE AND δ-VALUE, SUBSTRATE: ALUMINIUM.

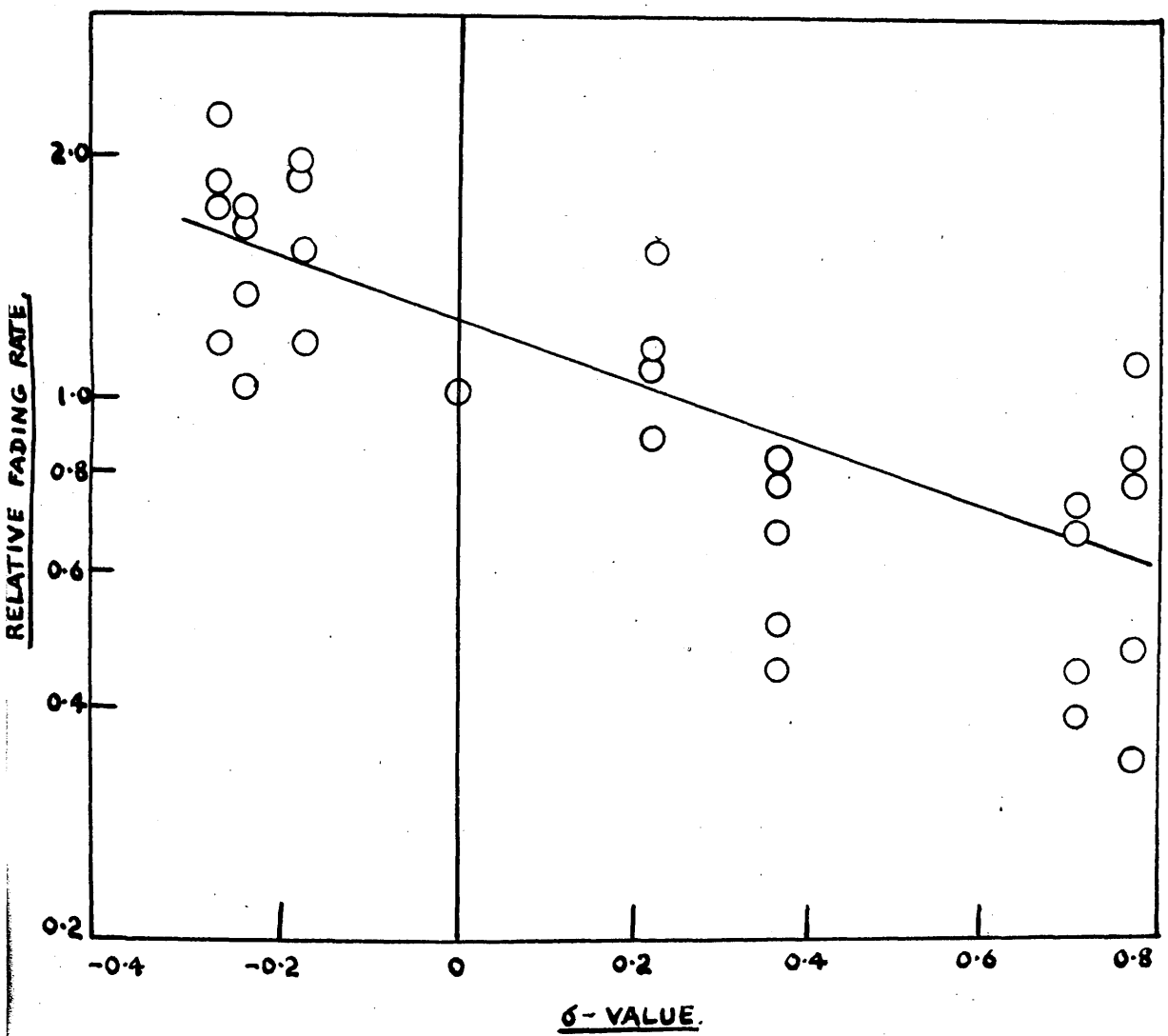


Fig II
RELATION BETWEEN RELATIVE FADING RATE AND δ-VALUE, SUBSTRATE: ASBESTOS.

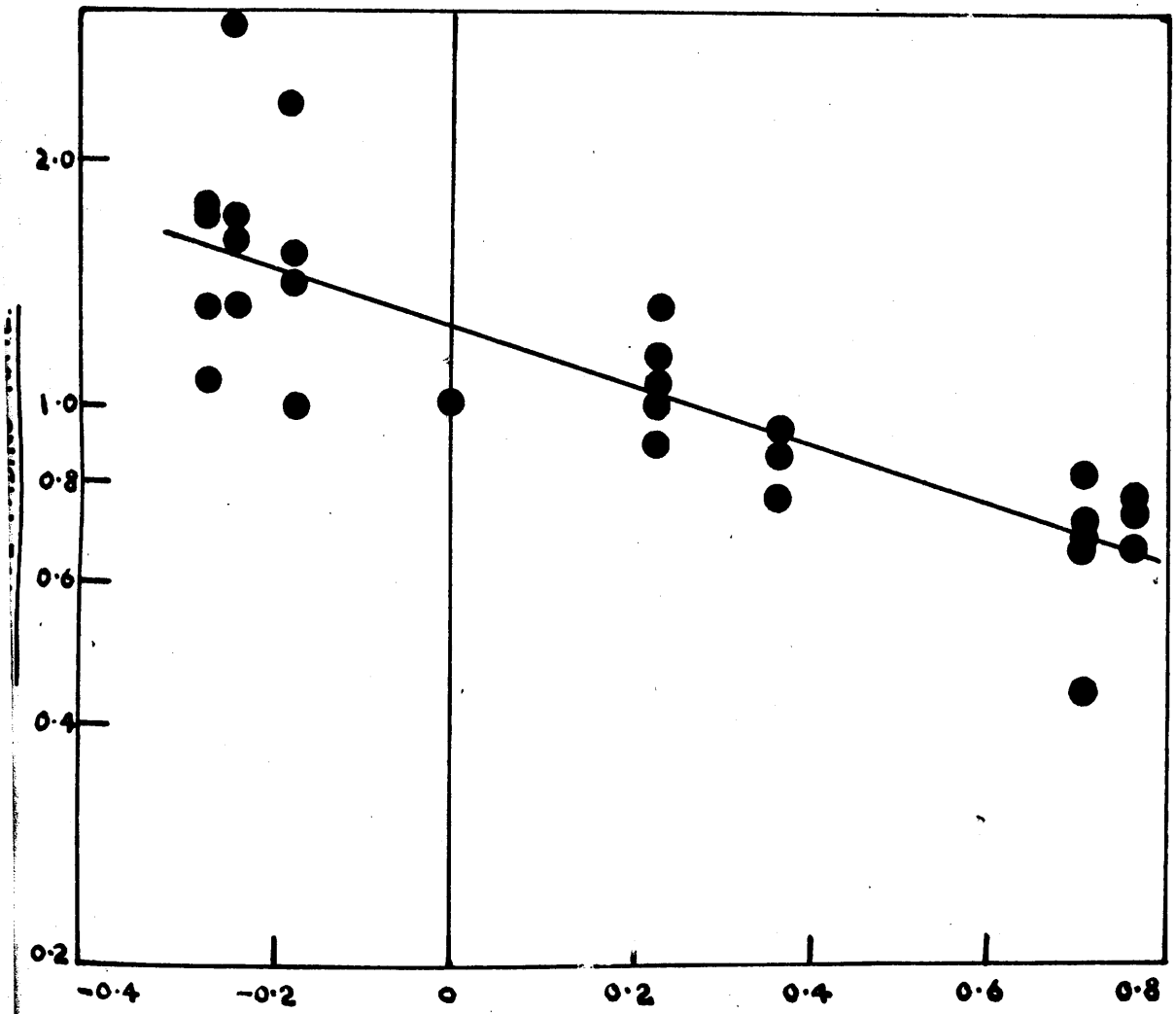


Fig. III
RELATION BETWEEN RELATIVE FADING RATE AND δ-VALUE, SUBSTRATE: CELLULOSE POWDER.

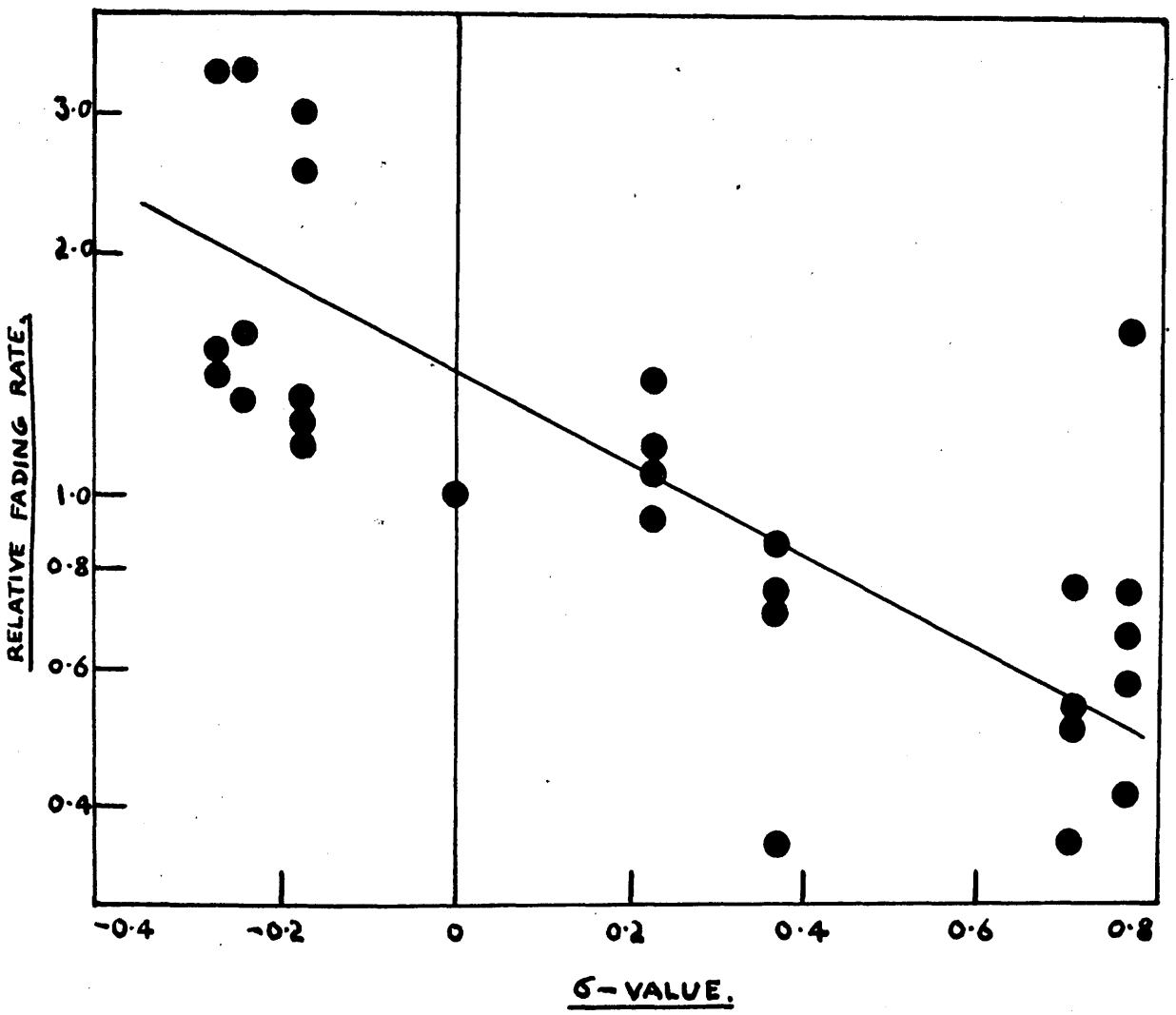


Fig IV
RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE: COTTON.

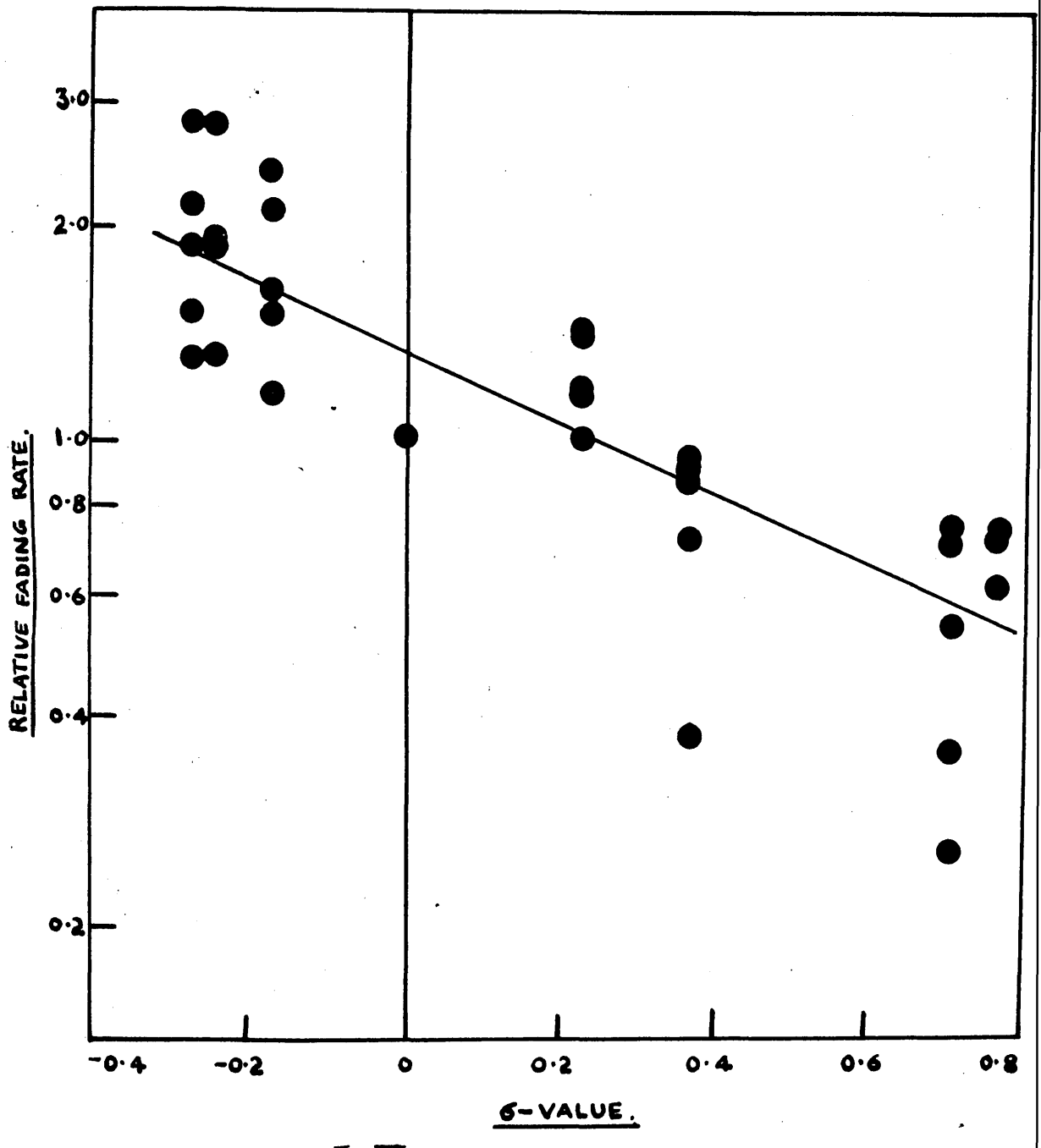


Fig V

RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE: PAPER.

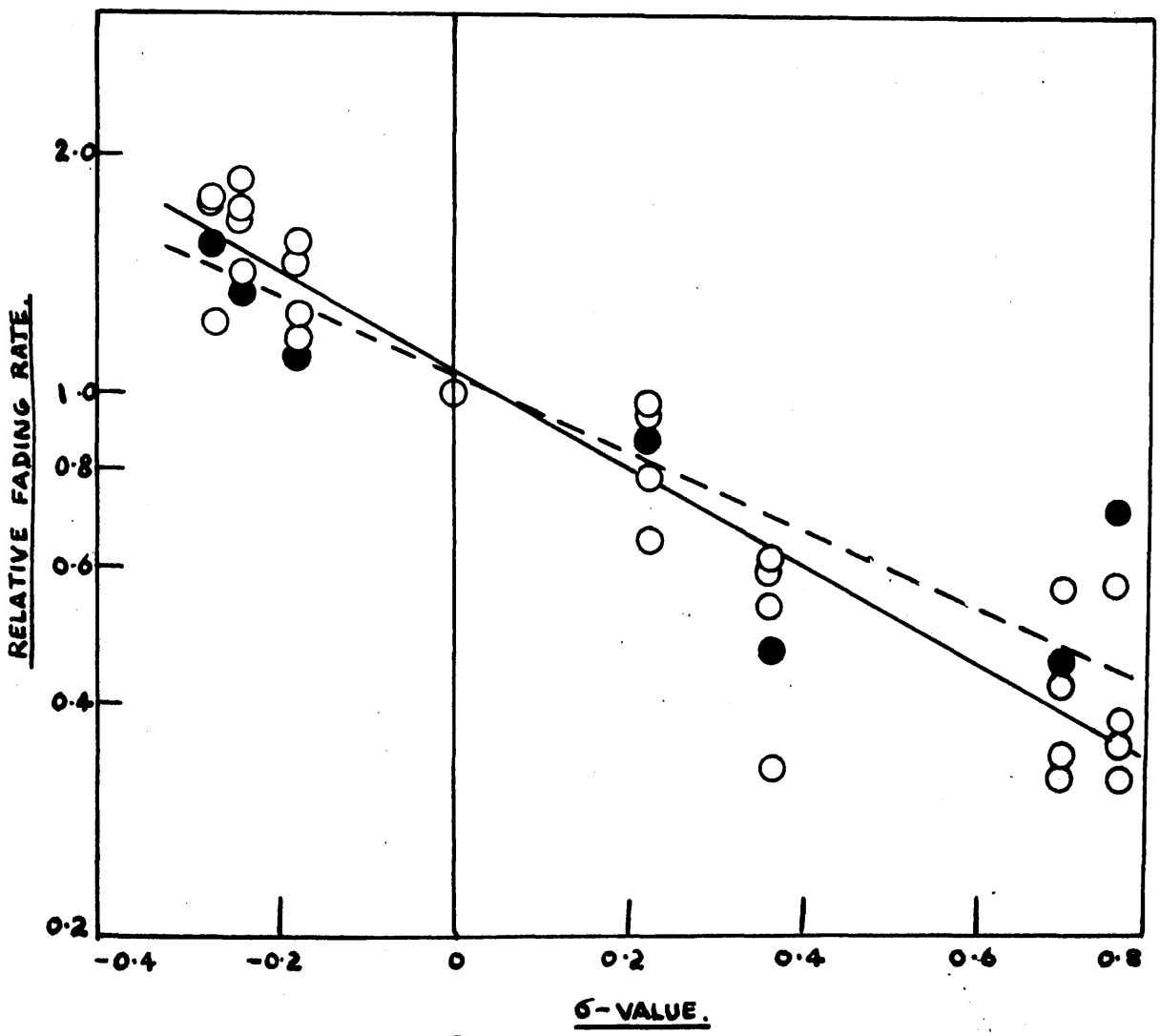


Fig. VI
RELATION BETWEEN RELATIVE FADING RATE AND δ-VALUE, SUBSTRATE: "CELLOFAS A".
– –●– – FADED AT 3650 A.

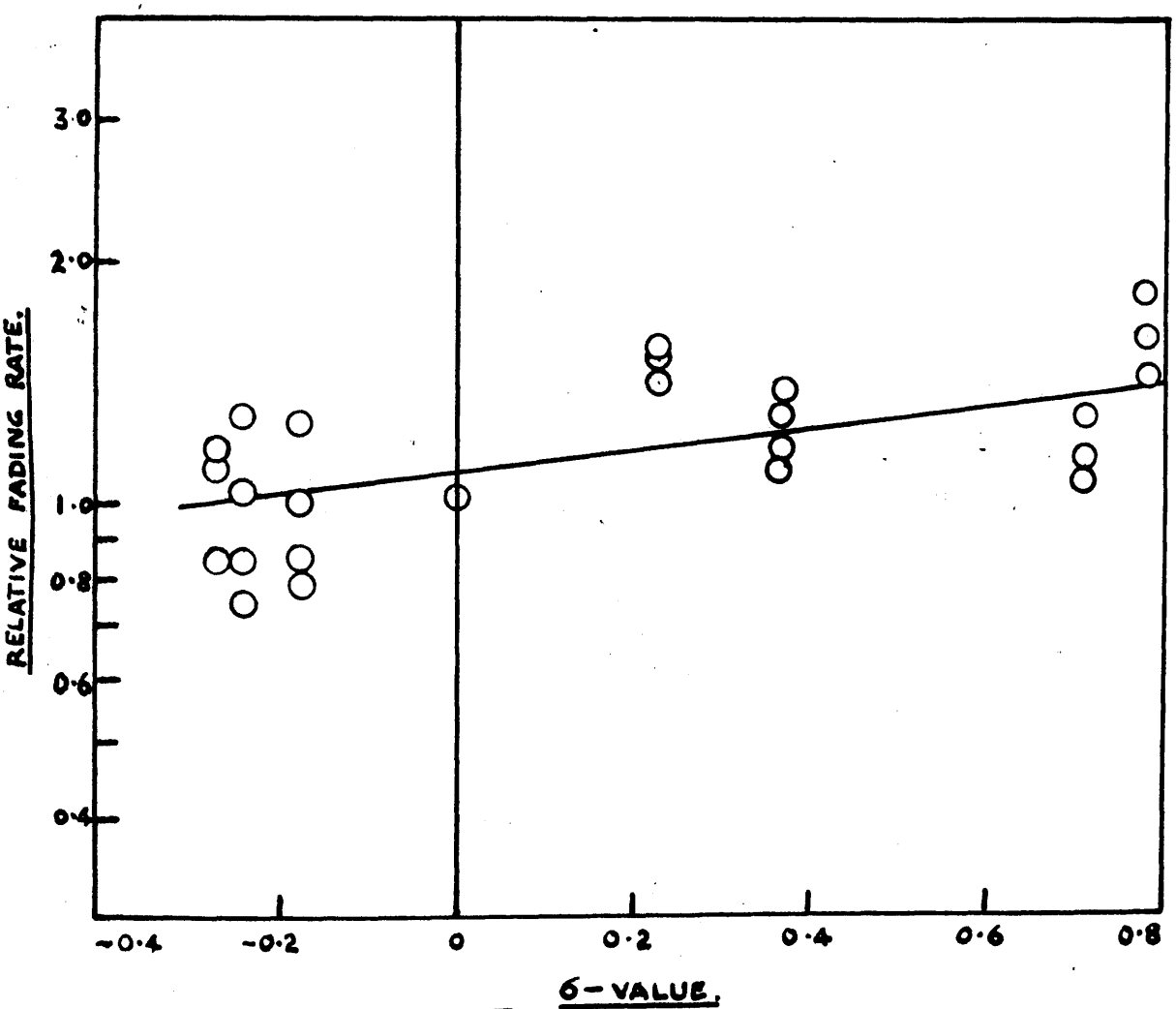
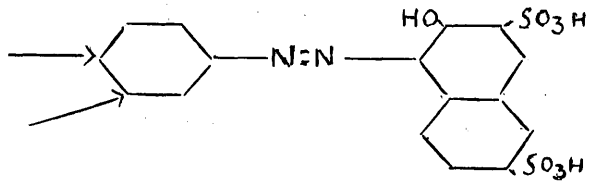


Fig. VII

RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE: GELATINE.

Table 1.

Purity of the R-acid dye.



R =	'6' value	Percentage purity: Titanous-chloride method	Percentage purity: Corrected for moisture content
H (aniline)	0	100.9	100.9
m-NO_2	0.710	86.6	99.0
p-NO_2	1.27	85.6	96.0
m-Cl	0.373	80.9	99.9
p-Cl	0.227	91.2	104.0
p-CH_3	-0.170	85.4	92.7
o-Cl		88.2	99.6
2:4 di-Cl		89.0	102.5
o-NO_2		86.8	97.0
o-COOH		79.1	86.0
m-SO_3H		76.1	86.0
p-SO_3H		69.8	80.5
p-OCH_3	-0.268	47.42	
p-OC_2H_5	-0.250	72.41	
p-$N(CH_3)_2$	-0.205	51.8	

Table 2(a)

Oxidation of R-acid dyes by H_2O_2 at pH = 8.85 (25°C.)

Dye (Table 1) R =	Time Hrs.	Time Min.	Percentage unoxidised
H (aniline)	1	10	72.76
	3	30	45.46
	5	15	28.92
p-NO_2	1	13	81.82
	3	38	60.01
	5	23	45.46
	6	23	27.27
m-Cl	1	20	87.50
	3	40	75.00
	5	25	62.50

Table 2(b)

Oxidation of R-acid dyes by H_2O_2 at pH = 8.85 (25°C.)

Time		Percentage unoxidised Dye (Table 1) R =		
Hrs.	Min.	m-Cl	p-Cl	p-CH_3
1	10	92.59	89.36	80.44
1	40	90.74	85.11	77.18
2	10	83.34	82.98	69.57
2	40	81.48	80.86	64.13
3	20	72.73	72.34	60.87

Table 3.

Oxidation of R-acid dyes by H_2O_2 at pH = 9.01 (25°C.)

Time		Percentage unoxidised Dye (Table 1) R =				
Hrs.	Min.	H (aniline)	m-NO_2	m-Cl	p-Cl	p-CH_3
1	20	75.61	96.66	90.91	79.08	68.89
1	50	63.41	93.33	76.37	74.42	62.22
2	20	58.54	86.66	69.09	63.96	48.89
2	55	46.35	79.99	52.72	51.17	44.45
3	30	39.04	63.33	36.37	41.87	37.77

Table 4.

Oxidation of R-acid dyes by H_2O_2 at pH = 6.49 (25°C.)

Time		Percentage unoxidised	Dye (Table 1)		R =
Hrs.	Min.	H (aniline)	m-Cl	p-Cl	p-CH_3
1	0	93.90		97.77	89.58
2	25	87.80	98.30	97.77	87.50
4	0	70.73	94.93	90.0	68.82
4	50	34.14	74.57	33.33	39.61
5	20		64.40	49.07	37.48

Table 5.

Oxidation of R-acid dyes by H_2O_2 at pH = 3.92 (25°C.)

Time		Percentage unoxidised	Dye (Table 1)				R =
Hrs.	Min.	H(aniline)	m-NO_2	p-NO_2	m-Cl	p-Cl	p-CH_3
5	25	97.14	94.73	93.18	96.42	97.61	97.06
19	35	82.86	78.95	68.19	89.29	70.73	85.29
24	35	74.29	76.84	65.92	89.29	70.73	77.64
30	15	34.30	34.21	27.19	44.66	32.93	38.24
36	0	22.86	22.38	19.22	32.15	25.61	27.94

Table 6.

Oxidation of R-acid dyes by H_2O_2 at pH = 9.01 (25°C.)

Time		Percentage unoxidised Dye (Table 1) R =					
Hrs.	Min.	O-Cl	2:4-di-Cl	O-COOH	p-SO_3H	m-SO_3H	o-NO_2
2	10	50.65	51.94	88.31	60.41	73.11	67.22
3	20	37.74	34.84	81.82	53.75	55.85	49.18
4	25	21.79	22.11	74.55	41.25	44.46	41.21
5	40	13.22	15.67	63.64	31.24	35.64	29.18
		----- 2nd set -----					
2	5	51.61	40.33	80.68	62.07	57.69	59.17
3	10	31.63	27.37	64.83	53.45	48.08	39.19
4	15	21.62	16.99	41.01	39.66	31.55	26.21
5	35	14.53	10.07	25.27	25.87	21.16	14.87

Table 7.

Oxidation of R-acid dyes by H_2O_2 at pH = 6.5 (25°C).

Time		Percentage unoxidised Dye (Table 1) R =			Time		Percentage unoxidised Dye (Table 1) R =		
Hrs	Min	O-Cl	2:4-di-Cl	o-NO_2	Hrs	Min	O-COOH	p-SO_3H	m-SO_3H
1	0	45.50	42.73	42.89	1	35	97.44	52.78	69.12
1	15	36.66	29.91	38.41	4	20	78.28	9.72	22.07
1	38	33.66	28.20	28.97	5	5	69.23		20.44
			----- 2nd set -----						
0	45	41.22	40.08	41.44	1	37	94.44	60.01	
1	5	34.20	32.06	35.52	3	47	65.28	21.00	
1	25	32.46	28.85	32.24	4	30	59.72	3.42	

Table 8.

Oxidation of R-acid dyes by H_2O_2 at pH = 3.92 (25°C).

Time		Percentage unodixised Dye (Table 1) R =					
Hrs.	Min.	O-Cl	2:4-di-Cl	O-COOH	p-SO_3H	m-SO_3H	o-NO_2
1	10	93.92	87.01	88.89	91.95	98.68	92.21
2	40	75.78	81.05	71.37	82.76	84.21	83.11
5	8	64.38	67.54	60.14	74.14	75.26	70.79
7	46	55.49	53.77	54.92	65.52	68.42	59.75
		----- 2nd set -----					
1	18	91.30	80.63	92.53	90.24	95.88	93.90
2	55	79.67	76.50	77.60	72.68	87.50	74.88
5	27	67.40	68.75	65.66	67.56	84.72	62.20
8	12	47.82	46.25	50.74	52.45	66.66	39.27

Table 9.

Rates of oxidation of R-acid dyes at 25°C. by H_2O_2.

(from Tables 2 to 8).

	Mean value of K x 10^{-5} for the dye (Table 1) R =					
pH=	H(aniline)	m-NO_2	p-NO_2	m-Cl	p-Cl	p-CH_3
8.85	7.626	---	4.919	2.319	2.533	4.582
9.01	6.777	2.301	---	4.965	6.038	8.334 (7.601)
6.49	2.001			a)0.2778 b)1.989	a)0.5365 b)4.860	a)2.395 b)5.217
3.92	a)0.2251 b)1.0608	a)0.3035 b)1.069	a)0.4589 b)1.2325	a)0.1584 b)0.8079	a)0.2836 b)1.037	a)0.2183 b)0.9330

Table 10.

Rates of oxidation of R-acid dyes at 25°C. by H_2O_2.

(from Tables 2 to 8).

	Mean value of K x 10^{-5} for the dye (Table 1) R =					
pH =	O-Cl	2:4di-Cl	O-COOH	p-SO_3H	m-SO_3H	O-NO_2
9.01	8.828	a)11.78 b) 8.771	a)4.834 b)1.959	5.912	a)7.535 b)5.004	a)8.362 b)5.656
6.5	22.45	25.99	a)0.4565 b)0.9813 c)1.575 d)2.10 e)3.133 f)3.182	a) 3.775 b)11.21 c)11.47 d)14.94 f)20.84	8.281	22.01
3.92	2.184	2.144	2.426	1.928	1.254	a)1.897 b)2.782

K = reaction rate

Ko= reaction rate of aniline ⟶ R acid dye.

K-values have been calculated on the assumption of the first order reaction since H_2O_2 was in large excess. As seen from the Tables many of the dyes are oxidised in two stages, the second stage being much faster than the first. In plotting log.(K/Ko) vs. '6' value (Figs.1 to 3) initial value is taken into account at pH = 6.49 while both the values are plotted independently with pH = 3.92 and shown with respective subscripts. In any case the expected order is obtained.

(Ref. New Set Tables 11 to 14).

Table 11.

Oxidation of R-acid dyes by H_2O_2 at 25°C.

pH = 9.01

Time		Percentage unoxidised for the dye (Table 1). R =					
Hrs.	Min.	H	m-NO_2	p-NO_2	m-Cl	p-Cl	p-CH_3
1	-	98.95	87.27	93.18	96.72	88.79	89.52
2	-	72.92	73.64	80.13	75.40	68.25	69.36
3	-	(50.50)	63.63	59.09	67.22	56.35	53.23
4	-	54.17	55.46	59.09	55.74	53.18	51.61

Table 12.

Oxidation of R-acid dyes by H_2O_2 at 25°C.

pH = 6.49

1	-	71.37	77.56	51.69	76.92	58.83	71.42
2	-	46.30	63.24	28.10	47.44	37.09	49.29
3	-	26.23	50.01	16.01	34.63	17.90	33.79
4	-	7.70	34.91	10.11	20.82	6.39	13.38

Table 13.

Oxidation of R-acid dyes by H_2O_2 at 25°C.

pH = 6.49

Time		Percentage unoxidised for the dye (Table 1). R =					
Hrs.	Min.	H	m-NO_2	p-NO_2	m-Cl	p-Cl	p-CH_3
1	-	78.23	79.06	48.53	83.10	69.25	65.01
2	-	43.81	71.43	30.50	57.72	53.19	60.42
3	-	25.16	45.12	20.21	51.60	23.00	37.16
4	-	9.88	36.55	16.32	44.02	24.64	33.58

Table 14.

Oxidation of R-acid dyes by H_2O_2 at 25°C.

pH = 3.92

6	-	76.45	79.11	71.42	68.29	77.78	72.97
12	-	(44.33)	44.76	43.47	51.23	(39.51)	49.76
18	-	48.93	43.28	39.33	47.57	46.17	45.95
24	-	37.62	42.14	39.33	45.12	37.78	34.33

Table 15.

Rates of oxidation of R-acid dyes at 25°C. by H_2O_2.

(from Tables 11 to 14).

pH	Mean value of K x 10^{-5} for the dye (Table 1) R =					
	H	m-NO_2	p-NO_2	m-Cl	p-Cl	p-CH_3
9.01	4.3165	4.171	3.277	3.88	5.302	5.166
6.49	10.80	6.779	17.19	10.346	14.8	9.728
6.49	12.11	7.351	15.32	6.081	10.11	9.240
3.92	1.175	1.140	1.516	1.355	1.176	1.244

Repeated experiments described in Tables 2 to 8 after attempting the purification of the new samples of dyes through the ion exchange resins. Considerable change in K-values is being noticed, however the general slope of the line log.(K/Ko) vs. '6 ' value (c.f. Figs.1 to 3) is not changed, which is the prime factor of the discussion; hence the individual values of 'K' have not been given much importance nor an attempt made to determine them under more ideal conditions. The above quoted values of K are the mean of those which agree well within the experimental error, (neglecting the other values).

Table 16.

Mean light fastness of R-acid dyes on Wool, Silk and Nylon. (Arc light figures).

(a) Wool	Exposure conditions			
Dye (Table 1) R =	Acid	Alkaline	Neutral	H_2O_2
H (aniline)	4.5	4.25	5.0	4.6
m-NO_2	4.0	4.0	4.25	4.2
p-NO_2	3.5	2.0	4.0	4.0
m-Cl	4.5	3.5	4.75	4.5
p-Cl	4.3	4.15	4.60	---
p-CH_3	4.5	5.0 ?	4.40	5.0
o-Cl	1.5	1.5	1.5	1.5
2:4-di-Cl	1.5	1.5	1.5	1.5
o-COOH	5.0	4.0	6.0	5.5
p-SO_3H	4.25	3.5	6.0	4.5
m-SO_3H	5.5	3.0	4.0	4.25
o-NO_2	6.0	4.5	---	6.0
(b) Silk				
H (aniline)	5	4.4	5.18	5.5
m-NO_2	4.25	3.5	4.5	4.75
p-NO_2	4.5	3.0	4.75	5.15
m-Cl	4.4	4.0	4.4	5.15
p-Cl	5.15	4.15	4.62	5.0
p-CH_3	5.75	4.0	5.03	5.0
(c) Nylon				
H (aniline)	3.25	3.0	3.25	3.0
m-NO_2	3.5	3.25	4.45	5.0
p-NO_2	5.75	3.40	4.15	3.25
m-Cl	5.0	5.75	5.1	6.0
p-Cl	---	3.5	5.45	3.5
p-CH_3	---	6.0	4.75	4.0

Table 17

Light fastness grading of Aniline-R-acid dyes on Silk and Wool.
Arc light exposures corrected to daylight.

Dye (Table 1)	Substrate and Conditions							
	Silk			Wool				
R =	Acid	Neut	Alk	Acid	Neut	Alk	Pyr	H_2O_2
H	5.0	5.2	4.4	4.5	5.0	4.3	2	4.6
m-Cl	4.4	4.4	4.1	4.5	4.8	3.8	1.6	4.5
p-Cl	5.2	4.6	4.3	4.3	4.6	4.3	1.8	---
m-NO_2	4.3	4.5	3.8	4.1	4.3	4.1	1.2	4.2
p-NO_2	4.5	4.8	3.4	3.8	4.1	2.5	1.1	4.1
p-CH_3	5.8	5.0	4.1	4.5	4.4	5.0	---	5.0

N.B. Pyr:- Pyruvic acid treated and exposed over it.

Table 18.

Mean light fastness of R-acid dyes on Aluminium, Asbestos and Cellulose powder. (Arc light figures)

Dye (Table 1) R =	Aluminium	Asbestos	Cellulose powder
H (aniline)	2.0	2.0	2.7
m-NO_2	3.15	3.0	4.15
p-NO_2	3.2	2.5	4.0
m-Cl	2.2	1.6	4.1
p-Cl	3.1	1.0	3.6
p-CH_3	2.15	1.0	4.25

Table 19.

Mean light fastness of R-acid dyes on Cotton and (insol.) ß-naphthol dyes on paper. (Arc light figures)

Dye (Table 1) R =	Cotton	Paper (0.01% soln. used)
H (aniline)	4.8	3.7
m-NO_2	5.8	4.5
p-NO_2	5.4	4.25
m-Cl	5.6	4.6
p-Cl	5.0	4.4
p-CH_3	6.0	3.9
p-OCH_3		3.6

Table 20.

Mean light fastness Insol. ß-naphthol dyes developed on wool. (a) Arc light figures (b) Hg.-vap. light figures with B.S.I. stds. and (c) Hg.-vap. light (without B.S.I. stds.) time for just perceptible change.

Dye (Table 1) R =	a (corresponding to 2% shade)	b	c	
			Hrs.	min.
H (aniline)	4.7	4.6	60	-
m-NO_2	4.8	4.0	28	-
p-NO_2	4.4	4.1	32	-
m-Cl	4.8	4.3	52	-
p-Cl	5.1	4.9	66	-
p-CH_3	3.0	2.7	7	30
p-OCH_3	3.6	4.0	20	-

Table 21.

Mean light fastness of the self-coloured wool, e.g. diazotised bases coupled with wool.

Substituent in the base R =	Arc light	Hg.-vap. light (shorter period of coupling)		Hg.-vap. light	
		Hrs.	min.	Hrs.	min.
H (aniline)	3.1	-	10	1	30
m-NO_2	4.5	25	0	24	0
p-NO_2	5.0	36	-	36	30
m-Cl	4.0	-	20	8	20
p-Cl	4.2	-	10	-	-
p-CH_3	1	very fugitive		1	30
p-OCH_3	<1	less than		1	0
p-OC_2H_5	>1	10 min.		1	0
p-$N(CH_3)_2$	<1			1	0

Table 22.

Mean light fastness of R-acid dyes (0.1%) on Aluminium and Paper (Hg.-vap. light) (a) with B.S.I. stds. (b) Time for just perceptible change.

Dye (Table 1)	a		b			
R =	Aluminium	Paper	Aluminium		Paper	
			Hrs	min	Hrs	min
H (aniline)	2	4.0	4	10	23	5
m-NO_2	3.2	3.8	13	-	20	-
p-NO_2	3.0	3.25	9	20	15	-
m-Cl	2.6	3.25	7	-	11	20
p-Cl	2.3	3.0	4	10	9	20
p-CH_3	2.0	3.3	6	20	15	-
p-OCH_3	-	3.4	-	-	16	-
p-OC_2H_5	<1 (e.g.0.4)	3.25	1	30	13	-
p-$N(CH_3)_2$	1.0	2.6	2	40	8	-

Table 23.

Some miscellaneous experiments

(I) Mean light fastness of R-acid dyes (0.1% shade) on paper treated with (0.1%) (a) l-tyrosine (b) 3:5 di-iodo-tyrosine (c) p-amino benzoic acid.

Dye (Table 1) R =	Arc - light figures		
	a	b	c
H (aniline)	3.7	3	3.4
m-NO_2	4.0	4.0	4.2
p-NO_2	4.6	4.2	3.4
m-Cl	4.5	4.6	3.7
p-Cl	4.2	3.7	3.5
p-CH_3	4.5	4.5	4.2

Table 23 (contd.)

(II) Mean light fastness of R-acid dyes on wool treated with pyruvic acid (2.5%), squeezed and dried (not completely) and exposed over 25% soln.of pyruvic acid.

Dye (Table 1) R =	Arc-light	Hg.-vap. light (with B.S.I.stds.)
H (aniline)	4.1	1.5
m-NO_2	2.2	<1 (e.g. 0.65)
p-NO_2	1.0	<1 (e.g. 0.30)
m-Cl	3.2	1.0
p-Cl	3.5	1.2
p-CH_3	4.2	2.6

N.B. Both the results agree well with the previous one in so far as the slope of the line (n_o - n) vs. '6' value is concerned.

It was found that pyruvic acid even as dilute as 1% affects the fading rates.

Table 23 (contd.)

(III) Mean light fastness of Insol. ß-naphthol dyes padded onto wool from acetic acid.

Dye (Table 1) R =	Arc-light figures	
H (aniline)	5	
m-NO_2	5.0	
p-NO_2	5.0	
m-Cl		(No definite
p-Cl	5	conclusions
p-CH_3	5	
p-OCH_3	5	are possible)

(IV) When diazotised bases were coupled with silk in the same manner as with wool, the colour so developed faded in less than 10 minutes in all the cases.

(V) Cellofas B 691 (I.C.I.) gives roughly the same order of fading of R-acid dyes as on paper while gelatin gives the same order as that of wool. However Cellofas B with 0.25% tyrosine incorporated in it gives the reverse order in which p-NO_2 substituent was found to decrease the fastness of the dye. More detailed experiments on these lines are in progress (see Discussion). Cellofas A (methyl ethyl cellulose) gave the same order of fading as cotton. All these films were measured on the Spekker photometer (as described in the Experimental section) with suitable filter.

APPENDIX

Light fastness of R-acid dyes on Aluminium, Asbestos, Cellulose powder, Cotton and Paper. Hg.-vap. light. (Results repeated by NM).

I Aluminium

Dye (Table 1) R =	(Hrs.) Time for just perceptible change				
	Set No.				
	1	2	3	4	5
p-OCH_3	60	120	79	69	69
p-CH_3	79	-	104	104	79
H(aniline)	104	223	137	169	120
p-OC_2H_5	60	91	69	60	48
m-NO_2	240	364	591	633	836
p-NO_2	157	194	120	364	158
m-Cl	257	316	390	418	780
p-Cl	120	223	240	240	448

(Fig. 1)

II Asbestos.

Dye (Table 1) R =	(Hrs.) Time for just perceptible change Set No.				
	1	2	3	4	5
p-OCH_3	60	60	60	69	60
p-CH_3	69	69	60	69	69
H(aniline)	104	137	69	128	104
p-OC_2H_5	60	79	69	79	79
m-NO_2	240	208	181	181	158
p-NO_2	224	169	208	120	137
m-Cl	208	169	158	167	158
p-Cl	91	91	79	120	91

(Fig. II)

III Cellulose powder

Dye (Table 1) R =	(Hrs.) Time for just perceptible change Set No.				
	1	2	3	4	5
p-OCH_3	181	137	69	79	69
p-CH_3	157	104	91	60	79
H(aniline)	240	148	91	137	120
p-OC_2H_5	181	91	69	48	69
m-NO_2	339	223	208	208	148
p-NO_2	363	-	128	120	158
m-Cl	257	169	137	181	128
p-Cl	208	137	91	158	91

(Fig. III)

IV Cotton

Dye (Table 1) R =	(Hrs.) Time for just perceptible change				
	Set No.				
	1	2	3	4	5
p-OCH_3	137	60	128	69	181
p-CH_3	158	79	169	79	181
H(aniline)	194	208	194	240	276
p-OC_2H_5	148	60	120	69	79
m-NO_2	364	591	552	480	363
p-NO_2	295	128	480	418	363
m-Cl	257	277	552	340	316
p-Cl	169	148	208	208	257

(Fig. IV)

V Paper

Dye (Table 1) R =	(Hrs.) Time for just perceptible change				
	Set No.				
	1	2	3	4	5
p-OCH_3	91	91	79	69	91
p-CH_3	104	91	91	79	91
H(aniline)	169	194	104	194	137
p-OC_2H_5	91	104	79	69	69
m-NO_2	240	277	418	364	390
p-NO_2	240	316	148	-	-
m-Cl	187	223	277	277	148
p-Cl	120	169	104	137	120

(Fig. V)

Figs. VI and VII reprdduced from NM's work show the relative fading rate of the R-acid dyes on Cellofas A and Gelatin; the order of these conforms with that expected by the visual methods used in the present work.

REFERENCES

Allingham et al: Discussions of the Faraday Soc. 1954, 16, 92.

Arshid et al: J.S.D.C., 1953, 69, 11.

Ashton, Clibbens and Probert, J.S.D.C., 1949, 65, 650.

Ashton and Probert, J.Textile Inst., 1953, 44, T 1.

Atherton and Peters, J.S.D.C., 1952, 68, 64.

Atherton and Seltzer, J.S.D.C., 1949, 65, 629.

Biltz and Eggert, Veroffentl.wiss.Zentral-Lab. phot.Abst.Agfa. 1933, 3, 294.

Blaisdell, J.S.D.C., 1949, 65, 618.

Blum and Spealman, J.Phys.Chem., 1933, 37, 1123.

Boguslovsky and Sadov, J.S.D.C., 1952, 68, 269.

Brownlie, J.S.D.C., 1902, 18, 295.

Burawoy, Salem and Thompson, J.C.S., 1952, 4793.

Burgess, Chem.and Ind., 1952, 78.

Collins, private communication.

Couper, Text.Res.J., 1951, 21, 720.

Desai N.R., Ph.D. Thesis, Glasgow University, 1951.

Desai and Giles, J.S.D.C., 1949, 65, 586.

Egerton, J.S.D.C., 1947, 63, 161; 1948, 64, 336; 1949, 65, 764.
J.Textile Inst., 1948, 39, T 293, T 305.
Textile Res.J., 1948, 18, 659.

Everest and Walker, J.S.D.C., 1929, 35, 236.

Fierz-David, Blangey and Stre[illegible], Helv.Chim.Acta., 1946, 29, 1718.

Gebhard , Farben-Ztg., 21, 253 (Chem.Abs. 1911, 5, 1517).

J.Prakt.Chem., 84, 564 (Chem.Abs. 1912, 6, 983).

Z.angew.Chem., 23, 820; 26, 79; (Chem.Abs. 1912, 6, 155; 1913, 7, 1613;

J.S.D.C., 1918, 34, 74.

Haller and zierisch, Melliand Textilber, 1929, 10, 951;

Z.angew.Chem., 1940, 43, 209.

Hammett, Physical Organic Chemistry (New York and Lonond: McGrew Hill Book Co. Inc. 1940) Chap. VII

Harrison, J.S.D.C., 1912, 28, 225; 1914, 30, 206.

Hibbert, J.S.D.C., 1927, 43, 292.

Hillson and Rideal, Proc.Roy.Soc., 1953, A 216, 458.

Kautsky et al., Ber, 1933, 66B, 1588.

Kienle, Stearns and van der Meulen, J.Phys.Chem., 1946, 50, 363.

Kujirai, Bull.Inst.Chem.Research,Kyoto Univ., 1950, 23, 35 (J. Textile Inst., 1953, 44, A515).

Lamigan, J.Textile Inst., 1948, 39, T 285.

Lazarev, Z.physik.Chem., 1921, 98, 94.

Lead, J.S.D.C., 1949, 65, 723.

Macaulay N.(NM), Ph.D. Thesis Glasgow University, to be submitted.

Morton, J.S.D.C., 1949, 65, 597.

Marney, Hexagon Digest (I.C.I.Ltd.), No.3, p.7 (July 1948); No.9, p.23 (June 1950).

Mounier, T.I.B.A., 1931, 5, 121, 237, 353, 469, 585, 587.

Pinte and Millet, Bull.Inst.text.France, 1949, 9, 29.

Ricketts, J.S.D.C., 1952, 68, 200.

Roberts, J.S.D.C., 1949, 65, 699.

Rowe and Dangerfield, J.S.D.C., 1936, 52, 48.

Scholefield and Patel, J.S.D.C., 1928, 44, 268.

Seywitz and Mounier, Bull.Soc.chim., 1928, 43, 648.

Vickerstaff, Physical Chemistry of Dyeing. (Oliver and Boyd, London, 1950) Chap.X.

Whealan and Peat, J.S.D.C., 1949, 65, 748.

§§§§§§§§§§§

PART II.

MECHANISM OF DYE SORPTION ON WOOL AND NYLON.

(Sorption at organic interface .)

(A) Liquid Phase

SUMMARY

A number of organic compounds containing one or more of the ketonic, hydroxylic, amino, azo etc. groups were used for sorption experiments on wool and nylon from non-aqueous solvents e.g. benzene, ethanol, n-butanol, and a possibility was examined of hydrogen bonding of these groups with those in the fibres. A number of conditions are discussed for this phenomenon to take place, and the results examined accordingly. It was shown that only compounds capable of forming strong OH.....O bonds can be sorbed by this mechanism, while compounds like azobenzene, stilbene etc. are shown to be sorbed through van der Waals attraction. The effect of traces of moisture has been shown to interfere with such sorptions a great deal.

INTRODUCTION

Sorption studies in general are of immense value in the elucidation of the chemical nature of the sorbent. Textile materials have been subjected to this type of study very exhaustively for this reason.

Fundamental work by Astbury on the elastic properties of wool by X-ray diffraction; on nylon by Burns and Garner and by Marsden and Meredith on the importance of the crystalline and amorphous nature of fibres has contributed a great deal to the knowledge of the structure of the fibre-forming molecules. Thus fibres have long-chain molecules with a very high molecular weight of the order of 10,000 to 20,000 , laterally held by cohesive forces of weak secondary character, usually hydrogen bonds and van der Waals attraction, except in wool where ionic (salt-linkages) and disulphide linkages are also operative; these molecules pass through various stages of crystalline and amorphous regions i.e. they may for some part of their length have a regular lateral arrangment forming what are known as crystallites or micelles, while in other regions they may have random or amorphous orientation. There is no well defined boundary between these two regions of orientation. One long chain molecule may thus form a part of two or more micelles. The crystallites are arranged with their long axes lying approximately along the length of the fibre, but the degree of orientation may vary in different fibres. The crystallites contribute strength, rigidity and

chemical resistance, while the amorphous parts contribute flexibility, elasticity and chemical vulnerability to the fibre. A suitable compromise between these properties gives rise to useful textile properties in high polymers (see Fibres from Synthetic Polymers, Ed: R.Hill, Elsevier Pub.Co.1953).

When a fibre is placed in water it swells owing to the osmotic pressure developed internally. X-ray analysis shows, however, that the inter-atomic spacing of the crystalline portion is unchanged, from which it follows that osmotic forces are insufficient to separate the chains in the crystallites and all the swelling must take place in the amorphous intermicellar material. This results in a moving apart of the micelles to a point at which osmotic pressure is balanced by the elastic forces tending to restore the fibre to its original state. In this swollen state the intermicellar material forms an open network of a system of pores between the crystallites. Very little information is available on the pore size and micelle size of these fibres. In any case it seems quite probable that the pores usually are sufficiently large to permit of the passage of dye molecules whenever successful dyeing has been achieved.

These remarks apply equally to wool and other protein and polyamide fibres, which form an important family of textiles. Speakman made a study of the pore size of wool by indirect means and concluded that the crystallites have an average thickness of 230 $\mathring{A}$ with a surface area of about $1.6 \times 10^6 cm^2/g$.

of wool and are separated by pores having a diameter of 6 Å in the dry fibre and 41 Å in the water-swollen fibre. The cross-section of the dyed fibre when examined under a microscope shows the penetration of the dye right to the core of the fibre. Obviously the dye cannot have passed in through the unswollen crystallites; it must have diffused along the intermicellar pores. In other words, on placing the fibre in the dyebath, swelling takes place, resulting in enlargement of the pores through which the dye can then diffuse. Once inside the fibre, the dye must be fixed in some way in order to account for the progressive increase in exhaustion of the dyebath. It is at this point that the chemistry of the fibre becomes important.

It is an accepted fact that dyeing of wool with acid dyes essentially involves salt formation of the dye anions with the free basic groups of wool (see Vickerstaff, "The Physical Chemistry of Dyeing"). There is much experimental evidence to support this, e.g. the acid binding capacity of wool has been determined most frequently and with greatest accuracy in the case of hydrochloric acid and shown to be 0.82 m.equivalents of acid per g. of wool. Many acid dyes also give saturation values corresponding with this figure.

As mentioned already, dye anions can diffuse through the swollen intermicellar spaces and thus approach very closely the substituted ammonium groups (in acid solution) to form the salt link. They are unable to do so in the crystalline region;

this is shown by X-ray analysis (Astbury and Dawson). It is possible that they collect on the surface of the micelles in numbers equivalent to the ionised groups inside them. This is a point about which some uncertainty remains, for the above assumptions would specifically imply a very unstable electrostatic system. Two schools of thought have, in fact, developed, one supporting the Donnan equilibrium theory and the other the Gilbert-Rideal theory (c.f. Speakman and Peters, J.S.D.C., 1949, Oloffson, J.Polymer Sci. 1953).

Harris et al have shown that the titration curves of wool with different acids differ according to the nature of the anion. Further evidence in favour of definite association of the anions with proteins comes from the work of Sookne and Harris, who found that the electrophoretic mobility of silk particles in suspension in aqueous solution (buffered) is greatly affected by the nature of the anion present, the effect of picrate ions being particularly great. Moreover, Steinhardt, Fugitt and Harris, who studied the absorption of weak acids on wool, found that the amount absorbed far exceeded the equivalent of the basic groups in the fibre. Similar results were obtained earlier by Wilkinson and Tylor and by Speakman and Stott. These facts, and the large sorption of p-nitrophenol observed by them and the analogous behaviour of nylon and of cellulose acetate (Marsden and Urquhart) towards phenols suggests that the acids are attached to the amide groups by hydrogen bonding and van der Waals forces.

Thus the swelling of protein fibres in concentrated solutions of weak organic acids may be due to the reduction in the cohesive forces of the crosslinking hydrogen bonds between amide groups. There is a clear tendency for the affinity to increase with increasing molecular weight or introduction of polar groups which is the behaviour to be expected if the affinity arises from van der Waals forces between the dye and the fibre. The change in affinity on introduction of any group into an anion is roughly additive (Vickerstaff op.cit., pp.303 Table 64). Thus as Peters has suggested, and Vickerstaff and others have confirmed, the number of sites to which dye ions and the undissociated dye can be attached is far in excess of the number assumed by Gilbert and Rideal. Hence the sites in the fibre are of two types, namely those which are adjacent to the positively charged basic groups and those which are not. In acid solution the former sites are dominant while in neutral and heavily dyed states the latter predominate. The present work mainly concerns the latter type of sites, with particular reference to the polarity, the planarity and the size of the sorbed molecule.

Dyeing of nylon, as studied by Boulton is of particular interest from this point of view. Nylon can be dyed by both acid and direct dyes from acid baths and by direct dyes also from a neutral bath. Thus it can show a dual dyeing

behaviour, resembling wool and cellulose, so much so, that if dyed with direct cotton dyes it exhibits dichroism as does cellulose. With this point in view and also because it has no inert epicuticle, as found in wool (Gralén), nylon fibre has been examined side by side with wool whenever necessary.

PRESENT WORK

This work is an attempt to identify the non-ionic forces involved in sorption by protein and other polypeptide fibres, by the application of certain simple solutes to nylon, wool etc. under a variety of conditions. Phenols and certain alcohols were amongst the solutes used. The action of these materials on wool, under somewhat different conditions to those used here, has been studied by other investigators, whose conclusions are summarised below. The other solutes studied (Table 1) do not appear to have received much previous attention in this type of work, nor do organic solvents appear to have been used.

RELATED WORK PREVIOUSLY REPORTED

Barr and Speakman found that wool fibres undergo a pronounced lateral swelling and a small contraction in length when treated with phenol (molten or in concentrated aqueous solutions), the effect being reversible, so that the original dimensions are restored by thorough washing with water. Speakman also found that supercontraction of wool is inhibited by molecules smaller than n-butanol, larger molecules being incapable of negotiating the pores (ca. 6 Å). This has been contradicted by King, who, as a result of his vapour phase studies of alcohols on wool maintains that the observed differences between alcohols were due rather to rate effects and

energy dissipation difficulties than to the pore size. The present work, however, seems to confirm Speakman's interpretation. (Astbury and Dawson showed that 1-naphthol-4-sulphonic acid can impair the permanent set of wool but that molecules bigger than this are apparently unable to do so.)

Recently Elöd and Zahn have also disclosed the effects of certain treatments on the supercontraction of wool in solutions of phenols (and also of sodium hydroxide, sodium bisulphite and formamide). They used aqueous solutions (1-7%) of phenol, catechol, resorcinol, hydroquinone, o- and p-nitrophenols and salicylic acid. Consideration of X-ray patterns and physical properties such as swelling, anisotropy, double refraction etc. revealed that primary valencies (peptide links and cystine bonds) were unaffected, hydrogen bonds only being broken.

Pakshver, Mankash and Kukonkova determined length changes of undrawn, partly drawn and fully drawn nylon yarns in 2-4% aqueous phenol solutions and explained the observed reduction in the extension, with increase in draft, as due to the compacting of fibre structure, which reduces diffusion of solute into the fibre.

RESULTS AND DISCUSSION

Table 1 gives the summary of all the sorption results in the liquid phase. Such a study inherently involves a number of factors which decide the course of sorption. These are mainly:-

(a) the crystallinity and the pore size of the intermicellar spaces,

(b) the size and shape of the solute molecule (particularly if van der Waals attraction is involved),

(c) the affinity of hydrogen bonding groups in solute and fibre,

(d) the crosslinks normally present in the fibre and their flexibility,

(e) the nature of the solvent, and

(f) the presence or absence of a resistant 'skin' or cuticle (e.g. the epicuticle in wool) on the fibre surface.

Thus, to interpret the present results all these factors must be taken into account and an explanation sought in the light of their influence. Tables 2 to 18 give the detailed results for the compounds which are positively sorbed, and Figs.1 to 9 show their characteristic sorption isotherms.

(a) Fibre structure:

As already pointed out, very little information on the crystallinity and pore size of the present fibres is available.

Wool has a pore size of ca. 6 Å in the dry state and ca.40 Å in the wet state (Speakman) This difference must be due to the enormous swelling of wool in water, depending in turn on the size of its amorphous region and the number of its polar groups. Nylon, wool and silk have a content of about 5% , 8% and 16% polar groups respectively (Meredith). Dole and McLaren obtained a value of 71% for the crystalline content of drawn nylon and 63% for the undrawn fibre.

(b) Physical attraction:

No doubt the size and shape of the molecule will greatly decide the magnitude of this attraction (c.f. direct dyes on cotton Allingham et al, Faraday Society Discussions,1954,No.16), yet it may be possible that competition by the great excess of the solvent suppresses such an attraction on the part of the solute molecules, particularly small ones. It has already been pointed out that dye anions differ in their affinity depending on their molecular weight and the number of polar groups. Steinhardt and Harris made an attempt to correlate the shape of the anion with its affinity for wool and concluded that planar ions have a greater affinity than compact 3-dimensional or chain-like ions of the same molecular weight, although later they modified their view. But it seems from the present results in non-aqueous solvents, where ionic forces are completely absent, that such a consideration may well be significant.

(c) Hydrogen-bonding affinities:

The Table below gives approximate data for the abundance of some of the principal hydrogen-bonding and cross-linking groups in the fibres under discussion.

Table

Approximate Content of Polar Groups in Fibres

(m. equivalents per gm.)

Groups OH.....O OH.....O	- Fibre - Nylon (Refs. Vickerstaff,	Silk Haurowitz,	Wool Howitt and Traill
Acid	0.09	0.29	2.08
Basic	0.10	0.20	2.43
OH (alcoholic)	-	1.59	1.52
OH (phenolic)	-	0.73	0.26
S-containing	-	-	1.13
Peptide	8.85	11.84	8.62

All these groups (except the sulphur-containing groups) are capable of reacting with each other or with hydrogen bonding groups in solutes of the type under examination. The alkylamide group appears to react in the enolic form in non-aqueous solvents and in the keto-form in water (Arshid et al). Thus in the enol form it may be that both oxygen and nitrogen atoms can contribute to hydrogen bond formation while in the keto-form in water the carbonyl group is protected by the

solvent and thus rendered inactive. Flett by infra-red spectrophotometry has determined the free energy of formation of some intermolecular hydrogen bonds in carbon tetrachloride solutions. His calculations for NH.....O bonds vary from 0.7 to 2.75 kcals./mol. (60°C), and for OH.....O from 1.36 to 3.23 kcals./mol. (60°C). However, it is clear from his observations that an OH.....O bond has a higher free energy than one of NH...O type between similar compounds. Presumably the NH.....N bond has a still lower value. Davies quotes the following figures for bond energies (in kcal./mol.): OH.....O, 6 to 7; or 7 to 9; or 2 to 4; CH.....O, 2.0; NH.....O, 2.0; NH.....O, 1.9; OH.....N, 7.0; OH.....Cl, 1.7. (The bonds formed by phenol are the strongest of any of those examined). A similar result has been noted by Tsuboi.

(d) Cross-linkages:

The principal cross-linkages in the fibres under consideration are as follows:

Types of cross-links	Groups linked	Fibre
OH.....O (phenolic)	tyrosine	silk
OH.....O (alcoholic)	serine	silk
OH.....O and/or NH....O	peptide	nylon, silk, wool
NH.....O	amino, carboxyl	silk, wool
-S-S-	cystine	wool

In order that a fibre may be dissolved completely by a solute, the strongest cross-links must be broken by it and even then, entropy considerations, e.g. rigidity due to high proportion of crystalline material, may prevent solution. "A negative free energy of mixing large enough to break down the crystalline structure at temperatures substantially below the m.p. of a polymer cannot arise from the entropy considerations alone but must be augmented by a negative heat of mixing; this occurs only in polymer-solvent systems in which the energy of the polymer-solvent contacts is greater than that of polymer-polymer or solvent-solvent contacts they replace." (Walker) Thus nylon (and terylene) which is dissolved by m-cresol, formic acid, thioglycollic acid and phenol, has only peptide bonds as lateral linkages, which are easily replaced by the powerful hydrogen bonding agents. m-Cresol and thioglycollic acid do not attack the peptide backbone structure in silk in the same way, as the molecules are too big to get access to it through the compact silk fibre. (Lloyd and Garrod) Formic acid does seem to reach the peptide structure but fails to affect the phenolic OH.....O bonds of tyrosine and thus no solution takes place. On the other hand, wool has sulphur cross-linkages, which can be broken only by chemical decomposition (alkaline hydrolysis) and not by any organic hydrogen bonding compounds.

In Table 19, the results of dissolving nylon in various molten solutes have been summarised. The results may not be

of considerable importance but they do give a rough correlation with sorption results. (They take no account of the relation between m.p. of the polymer and b.p. of solvent.)

Interpeptide links:

A general survey of this subject covering certain soluble and insoluble proteins is given by Edsall (1954). It is usually assumed that these links are of -NH.....O=C- type in the crystalline regions of polypeptides and proteins. (Bath and Ellis; Robinson and Ambrose). There is evidence, however, that the amide group is completely planar, the C-N bond having partial double bond character (Pauling et al; Robinson and Ambrose), which implies that the group is partially enolic and hence the interchain peptide bonds are partially of OH.....O character. There is some evidence to support this in, e.g., the apparent greater stability of alkylamides in dry solvents (Arshid et al; Buswell, Rodebusch and Roy detected considerable enolisation of certain amides in CCl_4 by I.R. methods.) and that only the very strongest hydrogen-bond disruptive agents (e.g. phenol, formic acid) dissolve nylon. It should be noted, however, that it is only necessary for the interaction energies of like molecules i.e. solute-solute or solvent-solvent to be 2-3 per cent greater than those of unlike i.e. solute-solvent molecules to give a positive heat of mixing capable of inhibiting all solvent action (Walker).

(e) The nature of the solvent:

Certainly it is to be expected that the solvent will have a specific effect on the sorption process, by:-

(i) Competitive action towards the solute or the sorbent; association and solvation of the polar solute molecules in non-polar solvents. (See Fig.10).

This latter phenomenon may effectively happen even in the fibre by suppression of the polarity of the groups in the molecule through closer lateral bonding with peptide groups and also other hydrogen bonding groups in the substrate. In other words a sort of shrinkage effect so far as the intermicellar pore size is concerned may take place (see sorption of benzene page 68). This seems to be quite possible considering the work of Takenhiko, Shimanonchi and Sarrichino Nizushima who, considering the α- and β-forms of protein structures, proposed that since the energy differences in the two are very small, various combinations of α- and β-forms are possible having the same energy content, and that steric factors associated with the bulky side chains and the hydrogen bonds influence these configurations.

(ii) Inactivation of certain groups, e.g. keto-groups, both in substrate and sorbate in water and the disturbance in the keto-enol equilibrium referred to above.

(iii) Ionisation of amino and carboxyl groups followed by swelling of the fibre structure through solvation of the ions by the solvent (especially water). These effects will be absent in non-polar solvents, e.g. benzene

(f) The wool fibre cuticle:

It has now been established by electron microscopy and other studies that wool has a very chemically resistant outer cuticle (the epicuticle) which retards the entry of liquids, except where it is broken by mechanical action (Gralén; Lindberg). This is likely to affect the rate of sorption on wool, but not the equilibrium value.

Interpretation of the Present Results.

(i) Sorption from aqueous solutions:

As far as these experiments are concerned (Table 11,17 Fig.7) there would not be any mechanical barrier to the solute molecules entering the intermicellar pores and hence the sorption of these compounds would entirely depend on the balance of energies of interaction between the molecules of water, solute and solvent. Acetone, diethylamine, pyridine, phenol and hydroquinone are amongst the compounds used here. None of these probably would have enough van der Waals attraction, to be markedly sorbed, particularly in the presence of large excess of the solvent. Pyridine, acetone and diethylamine, all of which are miscible with water in all proportions, show no sorption on wool or nylon. Thus none of them has sufficient hydrogen bonding capacity with wool or nylon[§] to overcome their own solubility

§ The keto group in acetone has no apparent tendency to form such bonds in water - Arshid et al, c.f. (c), (e).

in water or the attachment of hydrophillic groups of wool and nylon to water.

On the other hand phenol and hydroquinone show considerable sorption. Phenol shows no tendency of reaching a maximum value as would be expected from its well known swelling action. The heats of sorption of phenol in either case (nylon or wool) are ca.3.5 to 4.5 Kcals./mol. which is typical of one hydrogen bond per molecule from aqueous solution. It was found that no sorption resulted on nylon from alkaline solutions of phenol; this is similar to Marsden and Urquhart's observation in the case of cellulose acetate. Thus the phenate ion is not sorbed.

Hydroquinone (see Table 17) shows a tendency to reach a maximum sorption value as the concentration of the solution is increased, which is to be expected since it is a bifunctional molecule capable of cross-linking the fibre molecules. There is much evidence (Gustavson) that hydrogen bonds are formed between the phenolic groups of vegetable tannins and peptide links. (A number of dihydric and trihydric phenols have been tried in the same manner and are found to exhibit their polyfunctionality, where steric factors were not involved, by a colleague of the author, the late D.G.M.Vallance, a detailed report of which work appears elsewhere). It may also be noted here that phenol sorption was found to be reversible; desorption could be easily achieved by raising the temperature to a higher value.

(ii) Sorption from non-aqueous solutions:

From the Table 1 it is seen that p-aminoazobenzene, anthracene, azobenzene, benzene, o-hydroxyazobenzene, methanol, ß-naphthol, p-nitrophenol, phenol, stilbene and water are sorbed from the dry solvents on both nylon and wool (see Tables 2 to 18) while many other compounds were not sorbed. First of all an attempt is made below to offer an explanation for the failure of the latter group of compounds in the light of the various influencing factors already discussed. Later the positive sorptions are discussed so that this may serve as the useful guide to selection or synthesis of new dyes or other chemical agents for this family of fibres.

Negative Results of Sorption:

The compounds used here can be classified as follows:-

(i) ketones,
(ii) alcohols and phenols,
(iii) amino compounds,
(iv) azo compounds,
(v) hydroxyazo compounds and others.

It may, however, be noticed that some of the compounds belong to more than one category mentioned above.

(a) Compounds with ketonic functional groups:

(Acetone, benzophenone, benzoquinone, methyl-ß-naphthyl ketone, 2-hydroxyanthraquinone, 2:3:4-trihydroxy benzo-

phe phe quinone).

The affinity of a small donor compound like acetone seems to be too low to permit measurable sorption[§§] while the next three compounds in the absence of a swelling agent seem to fail to negotiate the pores of wool and nylon (c.f. (d) and (e)). Also the conjugated system of double bonds is interrupted in all these cases.

Oxidative effects were detected in benzoquinone in dioxan solution (35°, 60° C.)

2-Hydroxyanthraquinone was too sparingly soluble in benzene to serve any practical purpose, while the saturated solution of the same in dry dioxan or n-butanol failed to give any sorption; so did solutions from ethanol (max. 0.2%). Ethanol seems to have been preferentially sorbed while in n-butanol and dioxan probably intermolecular attraction between solute molecules or solute and solvent molecules far exceeds the weak bonding capacity with the fibres. No doubt the molecular size will also be a difficulty in this case.

2:3:4-Trihydroxy benzophenone was not sorbed from any of the solvents used. The above reasons would apply here also. Besides, it would be internally chelated particularly in benzene.

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§§ It has been observed previously that acetone can form intermolecular hydrogen bond complexes with other simple organic molecules in dioxan though not in benzene and water (Arshid et al) but these tests show that even in dioxan it does not appear to have sufficient affinity to break the interchain bonds of nylon or wool.

(b) Alcoholic and phenolic compounds:

(n-Butanol, haematoxylin, α-naphthol, o-nitrophenol)

Speakman has shown that molecules larger than n-propanol are unable to penetrate the pores of the wool. Also in benzene association of the molecules is possible. α-Naphthol shows association (see Fig.10) while o-nitrophenol, owing to its chelation, cannot form an OH.....O link. Haematoxylin, which could not be used except in ethanol, has too big a molecule, and ethanol itself would probably be sorbed preferentially. In dioxan the refractometric method of analysis gave a good calibration curve but the solution tended to be very unstable, and so no sorption tests could be made.

(c) Amino compounds (primary, secondary and tertiary):

(Aniline, diethylamine, N:N-dimethyl-4'-amino-azobenzene and pyridine).

Aniline, diethylamine and pyridine have lower affinity, compared to the corresponding hydroxy compound (e.g. phenol or methanol) and are capable of forming only NH.....N bonds, while the remaining compound cannot penetrate nylon (some sorption is noticed with wool - see later).

(d) Hydroxyazo compounds and phenylhydrazine:

(Azoxybenzene, phenylhydrazine, p-hydroxyazobenzene, benzeneazo α- and β-naphthols, 4'-dodecyl-azobenzene-p-cresol.)

None of these has any affinity for the fibres because of

unsuitable size for van der Waals attraction. p-Hydroxyazobenzene is highly associated in concentrated solutioms and is solvated in dilute solution (Fig.10). The use of ethanol water (1:1) as the solvent for this compound does not seem to reduce this tendency for otherwise the water-swollen fibre would have shown some sorption. (In this case at least, water does not seem to form any bridging linkage - Mehta).

4'-Dodecyl-azobenzene-p-cresol would be expected to have large van der Waals attraction, yet it fails to show any positive sorption (even on nylon 69), no doubt due to the very bulky alkyl chain.

In the case of benzeneazo- α and ß-naphthols, the large molecular size and intermolecular attraction (and chelation also in the latter) seem to prevent any sorption in the absence of swelling agents. (It has been noted that alcoholic solutions of benzeneazo-ß-naphthol failed to colour wool permanently, but if a certain amount of water was used the colour could not be washed away (V.B.Chipalkatti, private communication).

(e) Miscellaneous compounds:

(Diphenyl, benzeneazo-m-toluidine and bis-phenylazobenzene).

Diphenyl, though structurally somewhat resembling stilbene shows no sorption. Similarly benzeneazo-m-toluidine, though like azobenzene, has no sorption. Thus an uninterrupted conjugated system of double bonds and planarity of the entire

molecule are essential features for sorption in the present circumstances, but if the molecule is too large to enter the pores of the fibres, sorption may still not occur. This must be the reason for the non-sorption of both the above two azo-compounds.

In conclusion it may be said that generally the results agree quite closely with predictions made on the lines indicated at the outset of the discussion.

Sorption of Phenols by Nylon and Wool.

Phenol itself is readily sorbed by wool (and nylon) from non-aqueous solution; it is clearly able to disrupt the inter-chain bonds between -CONH- groups, because if the solution is sufficiently strong (e.g. 20% in benzene) nylon is entirely dissolved (Fig.7 Tables 11 to 13). ß-Naphthol, though apparently unassociated (Fig.10) is sorbed only in traces (Table 18). The reason for this has not been further examined but it would appear from basicity considerations that the phenolic group in this compound has low hydrogen-bonding affinity.

The average heat of sorption of phenol (from ethanol) on wool varies from 20 to 15 kcals./mol. in the direction of increasing sorption. This figure is rather difficult to reconcile with the known data of phenol sorption but as Speakman and Stott (and also Wilkinson and Tylor)have shown that the low sorption heat of an undissociated acid is the resultant of the acid displacing water of solvation already present

in the fibre and the sorption of acid itself, it seems quite possible that high heats are involved in the present conditions because water displacement is not taking place. Similar results (high value for heat change) have been obtained for anodised aluminium by the author's colleague (Stewart: private communication) in sorption from dry non-polar solvents particularly when an aromatic-aliphatic system is involved.

This is also confirmed in sorptions from iso-octane, where wool shows some sorption at 30°C., while none is measurable at 50°C. The solubility of phenol in iso-octane however is too low (ca.0.2%) for reliable results to be obtained. No phenol was sorbed on wool at b.p. both from ethanol and iso-octane (0.2%). Chitin, which is intermediate between protein and cellulose in constitution, showed no sorption of phenol under dry conditions from iso-octane (Subramanian - private communication).

(Cotton and viscose behave similarly towards phenol from iso-octane; both show sorption).

An interesting feature of these experiments is that unless freshly prepared solutions are used each time, consistent results are not obtained. As a matter of fact the same solutions used week after week showed a progressive decrease in the sorption of phenol. Thus moisture sorbed from the atmosphere competes with the phenol by preferential sorption. Similar discrepancies were noticed by Harkins and Gass in sorption of stearic acid from benzene on metals.

p-Nitrophenol is sorbed on wool and nylon as is expected, but as seen from Fig. 6 nylon shows much enhanced sorption capacity since this compound can break lateral bonds and cause swelling of the fibre until it dissolves. No higher concentrations can be used, as the saturation value is reached at about 11 g./l. in benzene.

Wool on the other hand shows a maximum value of sorption and indeed lower values of sorption than this maximum at higher concentration. Thus it seems that this compound is not as effective a swelling agent in the case of wool under the conditions here.

Effect of Solvent on Sorption of p-Nitrophenol.

Comparative tests of sorption of p-nitrophenol on wool from benzene and ethanol show that from 1% solutions at 40°C. (Table 9) the amount sorbed from ethanol is about twice that sorbed from benzene, even though the solubility in benzene is much less than in ethanol. The difference thus appears to be due to the swelling action of ethanol on wool (as against benzene which as a matter of fact is suspected to do otherwise) because it promotes slight ionisation of the side chains of the proteins.

At b.p. the sorption from benzene and iso-octane was too low to measure.

Sorption of Methanol on Nylon and Wool.

Methanol is readily sorbed by nylon or wool from benzene

solution and interesting isotherms are obtained (Fig.4). Again high heats of sorption (on wool) are involved, e.g. 15 to 18 kcals.per mol. for reasons already explained. The isotherm at the higher temperature reaches a maximum and then falls. This appears to be due to increasing association of the solute molecules.

Sorption of Water on Wool.

The use of Karl Fischer titrations has enabled the sorption of water by wool from non-aqueous solutions to be determined readily. Individual experiments were made with a number of solvents (see Table 16) and isotherms determined using n-butanol. There seems to be some dependence of the rate of sorption (0.4996% solution from each of the solvents) on the solubility, as indeed it was found that no sorption of water from ethanol or methanol occurred while from a benzene-alcohol mixture (4:1) as much as 2.9 m.mols./g. were sorbed under identical conditions. (Bartell et al also find a correlation of water solubility in alcohols and monolayer capacity on silica gel). This point certainly needs further investigation.

The isotherm of water from n-butanol (Fig.9) is similar to that of the sorption of water vapour by this fibre. The conditions indeed are somewhat similar in the two cases, for the only molecules which can penetrate the fibre in the present

system are individual water molecules escaping as vapour from the solution; the molecules of the solvent itself are too large to enter.

The apparent heat of sorption is about 7 kcals.per mol. This seems to be far too high to be accounted for by van der Waals attraction and hydrogen bonds must therefore be formed between water and molecules of substrate. This value seems to agree with the value given by Cassie for stress-free isotherms on wool (e.g. 6.6 kcals./mol.). Thus it is apparent that stresses that would normally be produced due to bulk swelling in water are absent here (c.f. (e) above and sorption of benzene below).

Arshid et al find that water acts as a bridge compound between two CONH- groups in a non-aqueous solvent. If this is so, two hydrogen bonds are involved per water molecule. Some difficulty has been experienced in obtaining consistent results and smooth curves in water sorption experiments. This is believed to be due to traces of moisture sometimes remaining in the fibre, for results which are irregular show lower sorption values than the smooth curves of Fig.9.

Sorption of p-Aminoazobenzene, Anthracene, Azobenzene, Benzene and Stilbene.

Benzene like water remains in cotton in non-freezable form as shown by Magne and Skau. These authors have shown

that the non-freezing water capacity is in direct proportion to (i) permeability of dyes (ii) moisture regain (iii) heats of wetting (iv) rates of chemical activity etc., the properties which are associated with greater distention and thus greater available surface area. That benzene is sorbed in appreciable quantities from n-butanol shows that similar effects might be expected in wool as well, and indeed, taking into account its molecular size, it may well enter the pores of the wool in the dry state (as a vapour in the present experiment) and remain condensed inside, firmly bound by van der Waals attraction. Also comparing the sorption values of other compounds mentioned in the list above, which are also believed to be sorbed through van der Waals attraction, the high value for benzene is indicative of its entry into the intermicellar pores. However, at high concentrations of benzene, in n-butanol, sorption decreases; no explanation is to be found for this (Fig.3.).

As seen from Figs. 2, 8, wool shows identical behaviour towards azobenzene and stilbene both in the shape of the isotherm and the sorption values. The apparent heat of sorption for the former is of the order of 1.8 to 2.3 kcals./mol. There is great similarity in the two molecules (Birnbaum et al) in their planar structure, conjugated system and trans configuration. Thus van der Waals forces seem to be the only operative forces causing this sorption.

Nylon, no doubt, shows exactly similar behaviour towards

stilbene but rather different behaviour towards azobenzene. Its sorption values are far too low and tended to show greater temperature dependence. It is necessary to study the latter in further detail before any conclusions can be drawn.

It may be mentioned here that these solutions were sodium dried. Some earlier experiments without such drying showed rather inconsistent results in repetitive experiments (see Tables 3,4). Sorption on wool after drying the solution was increased by about 50% to 60%. Sorption of azobenzene from carbon tetrachloride, however, was only half the sorption at the same concentration from benzene, while from m-cresol none was sorbed.

Sorption of Azobenzene on Alkali-treated Wool and Nylon.

In both of the cases (see Fig.3) sorption has increased, the effect being more pronounced on wool. The epicuticle of wool, which is inert and electrical in nature, has high wettability towards weakly polar or non-polar solvents, becomes more polar on alcoholic potash treatment (Lindberg), thus its affinity for a completely non-polar solvent, e.g. benzene, is reduced, hence probably allowing the diffusion of weakly polar compounds like azobenzene into the pores, and their sorption on wool is increased. In other words in such circumstances benzene is less likely to depress the polarity of the fibre molecule and may thus not interfere with any possible hydrogen bonding.

In the case of nylon this effect is not well pronounced but does seem to exist.

p-Aminoazobenzene probably on account of its symmetry of molecule (and also less associating tendency) behaves in the same way as azobenzene, even though the sorption values are much lower. When the solution was not sodium dried, no sorption was noticed.

Anthracene, which is sorbed only in traces, must do so entirely by van der Waals forees, which are enhanced to a certain extent on account of the conjugated system of aromatic nuclei.

From the observations in the preceding pages and other general considerations, the following points are suggested.

(1) The NH.....N bond is incapable of breaking the inter-peptide bonds of nylon and wool.

(2) Ketonic groups either in the solute or sorbate are incapable of intermolecular hydrogen bonding, both in aqueous and non-aqueous solvents.

(3) High solubility of the sorbate in the solvent depresses its attraction for the sorbent unless very strong hydrogen bonding groups are present in the solute molecule.

(4) The molecular size and planarity of the molecule determine its sorbability.

(5) A non-polar solvent, e.g. benzene, which promotes inter-molecular association or intramolecular chelation also

seems to affect similarly the polar groups of the fibre, depressing their polarity to the maximum extent and preventing weakly bonding (NH.....N or OH.....O) groups from being effective.

Indeed, in certain cases, negative sorption occurs and the concentration of solute outside the fibre has increased after sorption e.g. n-butanol from benzene.

(6) The pore size of wool and nylon seems to be of the same order in the dry state.

EXPERIMENTAL

REAGENTS

All solutes were either commercial products of analytical quality or purified laboratory specimens. Benzene, ether and toluene were stored over sodium, the ethanol was commercial 'absolute' material (ca. 99% as determined by Karl Fischer titration), the dioxan and methanol were of the "specially dried" quality (B.D.H.) used for Karl Fischer analysis; the remaining alcohols were of analytical reagent quality, and distilled water was used for the aqueous solutions.

Benzeneazo-m-toluidine was prepared from diazobenzene, m-toluidine and m-toluidine-hydrochloride (Meyer, Ber. 54, 2273). A high melting by-product was obtained which was insoluble in petrol-ether. The soluble product recovered after evaporation of the solvent was recrystallised from iso-octane (m.p. 73°C.) into orange leaflets.

Bis-phenyl-azobenzene was prepared from p-aminoazobenzene and nitrosobenzene by the method of Mills (J.C.S., 67, 929). It formed orange crystals from glacial acetic acid m.p.168°C.

4'-Dodecylbenzeneazo-p-cresol was prepared from p-dodecyl-aniline and p-cresol by the method of Giles and Neustadter (J.C.S., 1952, 918). It crystallised from acetic acid, m.p. 35-40°C.

Haematoxylin was purified by simple crystallisation from water and drying under vacuum.

2-Hydroxyanthraquinone (commercial sample) was extracted with water for 4/5 hours to remove any mineral impurities and then recrystallised from alcohol.

o-Hydroxyazobenzene was prepared in small yield (ca. 1%) by steam distillation from a sample of p-hydroxyazobenzene.

Methyl-ß-naphthyl-ketone was prepared by Friedel and Crafts' reaction between resublimed naphthalene and freshly distilled acetyl chloride in dry nitrobenzene. (Vogel: Practical Organic Chemistry: 1948). The solid recovered after removal of nitrobenzene by steam distillation was crystallised from glacial acetic acid, m.p. 54°C.

Some of the non-hydroxylic solutes e.g. azobenzene and aminoazobenzene gave rather inconsistent results unless the solutions and not the solvents alone, were dried over sodium. Evidently traces of water sorbed on the reagents in the solid state or the solutions during storage interfere with sorption. Solutions of hydroxylic compounds could not be dried because they reacted or formed adsorption complexes with the drying agents. The solid solutes were therefore oven dried below their m.p.s over a long period.

All the non-aqueous solutions which were not dried by sodium were made up freshly before each experiment. If this was not done, inconsistent results were liable to be recorded particularly showing progressive reduction in sorption values; this is believed to be due to the absorption of traces of

moisture (c.f. p-hydroxyazobenzene and phenol in the discussion below).

Fibres: These were first purified as follows and then stored in well-stoppered bottles.

Nylon: (15 film 45 den. drawn yarn) was scoured in 0.5/100 solution of a non-ionic detergent (Lissapol N, I.C.I.Ltd.) with addition of a little ammonia, at 60°C. for 15 min. It was then thoroughly rinsed in running water, then in distilled water and dried.

Silk: (raw domestic) was degummed by boiling for 1 hr. in 3/100 soap solution, followed by similar treatment in soap solution (1/100) for 30 min. then by thorough rinsing and drying as before. Before use, traces of yellowish solvent-soluble colouring matter were (Soxhlet) extracted from the fibre by toluene.

Wool: (root ends, 1.5in to 2in.) of a Lincoln fleece was scoured as for nylon, then (Soxhlet) extracted with ether for 24 hrs., (or with methylenedichloride, which is more effective than ether in removing waxes and offers no fire hazard); then steeped overnight in running water, followed by thorough rinsing and steeping in distilled water and drying.

Before use, the above fibres were conditioned to room temperature at least for 24 hrs., weighed in the air-dry state, then oven dried at 100-110°C. for 12-18 hrs. and immediately introduced into the sorption liquors. The quoted weights are

those in the air-dry state.

Nylon 69: This was received in the form of lumps of a very hard resin m.p. 197-199°C. It was dissolved in phenol, precipitated in water, washed overnight in running water to remove phenol, rinsed in distilled water, dried and conditioned to room temperature before use.

Specially dried fibres: Some samples of wool (and nylon) indicated in Table 1 were dried by steeping for successive 12 hr. periods in 'absolute' ethanol, 'specially dried' methanol and dry ether, followed by oven drying at 100-110°C. for 4 hrs. They were then immediately introduced into the sorption tubes.

Alkali treatment of wool (and nylon).

This was done by the method described by Lindberg (J. Textile Res., 1953, 23, 67) using alcoholic potash, whereby only the surface of the wool is attacked and not the bulk. For comparison nylon was also treated similarly.

Preparation of Haematoxylin solution.

This was found to be soluble only in ethanol, amongst the dry solvents used here. Even then it showed a very rapid oxidative tendency, particularly in the presence of wool; hence the following precautions were taken:-

(i) Nitrogen was bubbled through the solution during its preparation

(ii) The same precaution was taken before introducing the fibre into the solution.

(iii) A blank experiment was always run side by side with the sorption experiment.

The lakes were formed in the usual way either from aluminium chloride or potassium chromate. A fairly good calibration line was obtained using a 'Spekker' photometer.

Sorption tests:

0.2 to 0.5 g. of fibre and 5-15 c.c.s of 0.1 to 10 g. per l. solutions were placed in closed containers, ground glass stoppered tubes (Quickfit) being used for aqueous solutions and completely sealed glass tubes for those in organic solvents (on account of the difficulty of preventing loss of solvent through the ground glass joints). The tubes were placed in a thermostat tank and mechanically agitated, end-over-end, under water at ca. 50 cycles per min.

The fibre was packed into a separate inner open-ended perforated tube. This falls to-and-fro during the agitation cycle, out of phase with the main container, so that the liquor is caused to pulsate in and out of the fibre through the perforated walls (Arshid et al). This simple device overcame the difficulty, otherwise experienced, of a mass of loose fibre blocking the sorption tube and preventing adequate contact with the solution.

Where positive sorption was noticed, the time required to reach equilibrium was determined at the required temperature

before proceeding with the isotherm study.

Methods of analysis:

Most of the aromatic compounds, and acetone, were determined absorptiometrically on a Hilger Spekker absorptiometer or a Unicam SP500. photoelectric spectrophotometer. The use of iso-octane as solvent, which has low u.v. absorption, enables a number of colourless compounds e.g. phenol, pyridine, stilbene etc. to be analysed in this manner. Volumetric methods were used for phenol (from water and ethanol), dihydric phenols (Pence's method - J.Ind.Eng.Chem., 1913, 5, 1218) and water; for the latter, Karl Fischer titration in a Townson and Mercer (B.D.H. pattern) apparatus was employed.

Some aromatic and aliphatic compounds whose analysis might otherwise have been difficult e.g. methanol or butanol in benzene, benzene in butanol, pyridine in water, were determined by a refractometric method (c.f. Arshid et al). The refractive index of the solutions after the test was measured on an Abbe refractometer and the extent of sorption determined from a calibration curve of the pure solutions. The square of the refractive index has a linear relation to the concentration of (dilute) solutions. A correction was applied for the slight change in the refractive index of the pure solvent in a blank experiment run simultaneously, attributed to traces of impurity or decomposition products from the fibres extracted in the prolonged sorption procedure. As an additional

precaution, the fibres were (Soxhlet) extracted for several hours prior to the experiment with the solvent to be used for the sorption tests.

It may be mentioned here that an attempt was made to estimate methanol by Karl Fischer titration (Aquametry: Mitchell and Smith, Inter Sci.Pub. N.Y., U.S.A. 1948, p.31). The method essentially involves esterification of methanol by acetic acid in the presence of a catalyst (borontrifluoride) and the estimation of water produced during the reaction. When this method was applied to dioxan solutions of methanol, the error involved was too high for it to be applied for the experiments in the present series; while in benzene solution a very low percentage of esterification was obtained.

Examination of azobenzene solutions:

Spectroscopic examination of the azobenzene solutions was made before and after the sorption tests, in comparison with solutions of azoxybenzene, in order to determine whether the reduction in concentration of the former might be due simply to a catalytic oxidation to the azoxy compound and not to sorption by the fibre. In the spectral range examined both the compounds have an absorption peak at 3300 Å and azobenzene has one at 4400 Å. It was not possible therefore to obtain decisive evidence, but the consistency of results and the absorption curves of the blank experiment did not

suggest that azoxybenzene was present after sorption. Oxidative effects were observed in the case of haematoxylin solutions in water, particularly in the presence of wool; haematoxylin in absence of fibre is fairly stable (Arshid eta al. unpublished). The author also noticed similar effects in aqueous solutions of haematoxylin and in solutions in ethanol (and dioxan).

Thermodynamic data.

The apparent heat of sorption, i.e. the resultant value of the heat generated by formation of the bond between solute and substrate and that generated by removal of solute from solution, was calculated by the Clausius-Clapeyron equation, from the equilibrium bath concentrations required to produce the same concentration of solute in the fibre at two temperatures. All the isotherms are plotted simply as equilibrium concentration in bath in g./l. vs m.mols/g. sorbed on the fibre.

Molecular weight determinations.

These were made by the Beckmann F.P. method in specially purified and dried benzene (B.D.H.) supplied for the purpose.

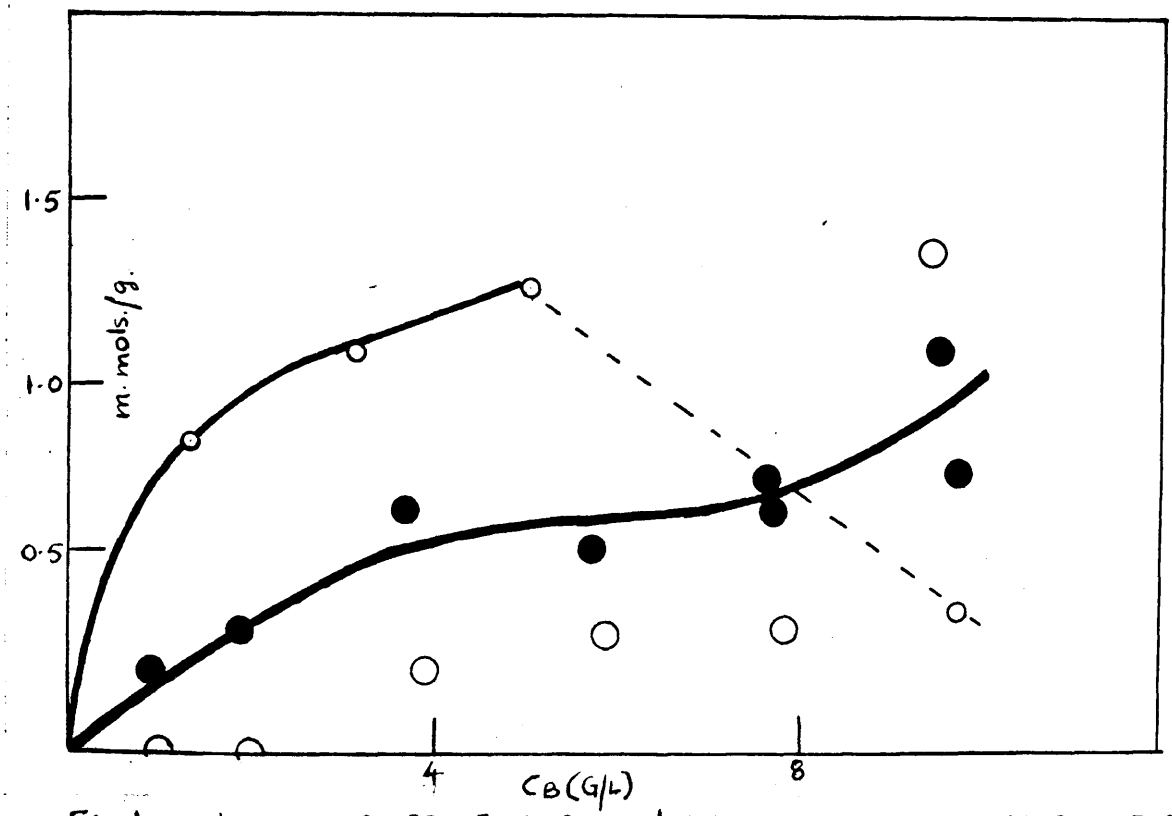

Fig. 1 p-AMINO-AZOBENZENE AND pN-N-DIMETHYL-AMINO-AZOBENZENE ON WOOL FROM BENZENE

○ p-AMINO-AZO-BENZENE 50°
● p-N·N-DIMETHYL -do- 30°
○ -do- 50°

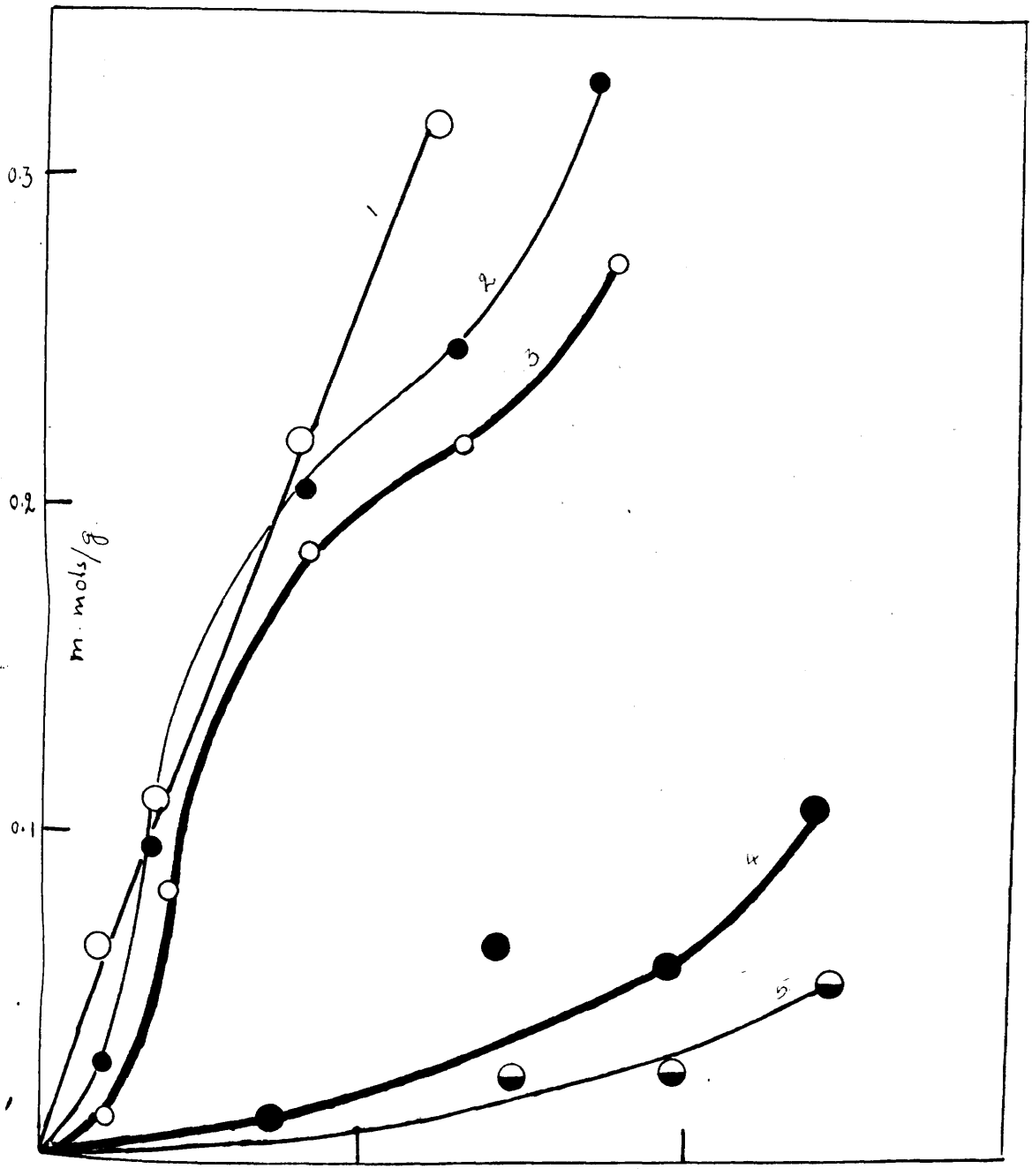

Fig. 2 AZO-BENZENE FROM BENZENE ON NYLON AND WOOL

1. WOOL (KOH TREATED) - 50°
2. WOOL - 30°
3. WOOL 50°
4. NYLON (KOH TREATED) - 50°
5. NYLON 50°

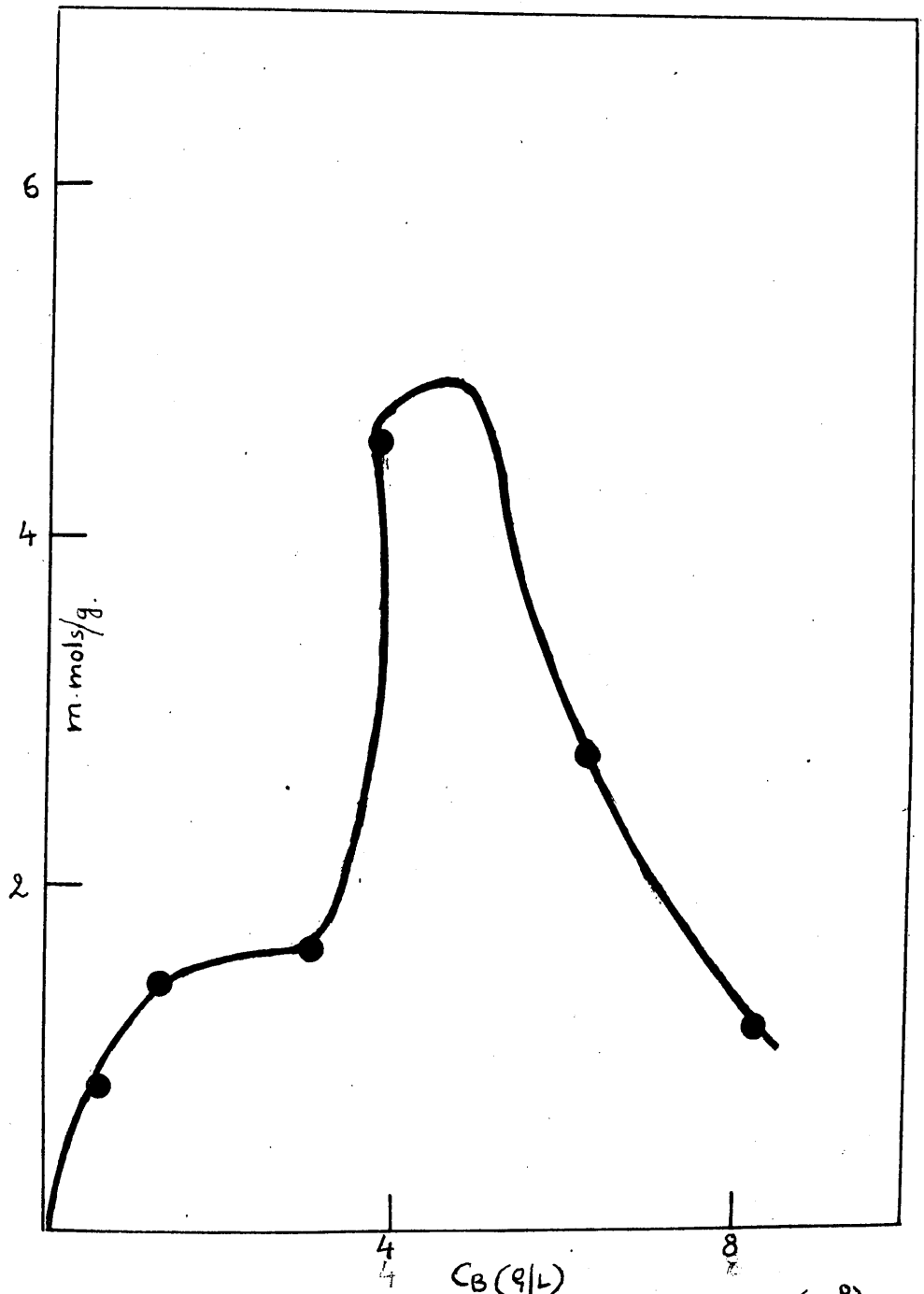

Fig. 3 BENZENE ON WOOL FROM n-BUTANOL (50°)

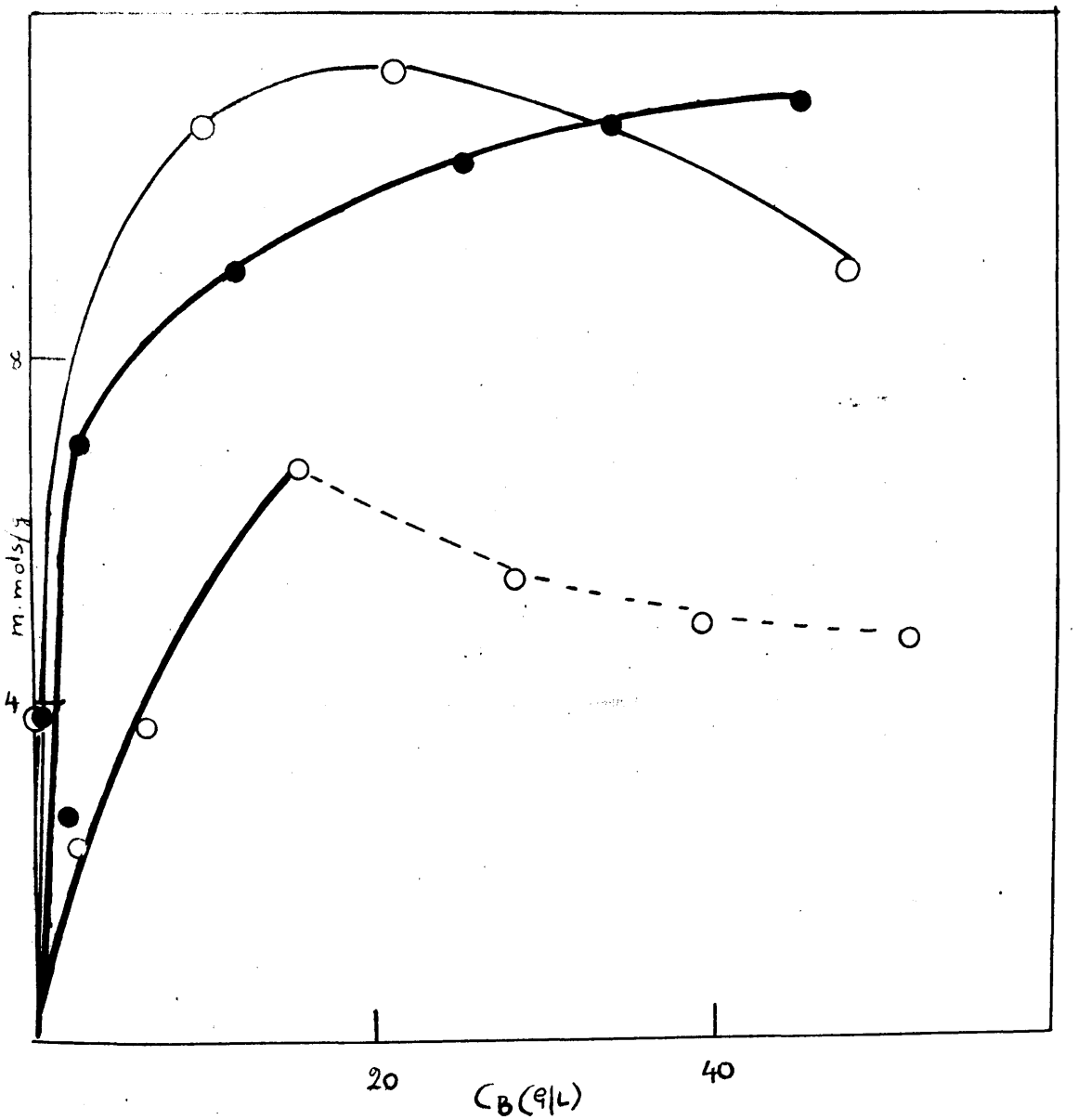

Fig. 4 METHANOL FROM BENZENE ON NYLON AND WOOL

1. NYLON 50°
2. WOOL 30°
3. WOOL 50°

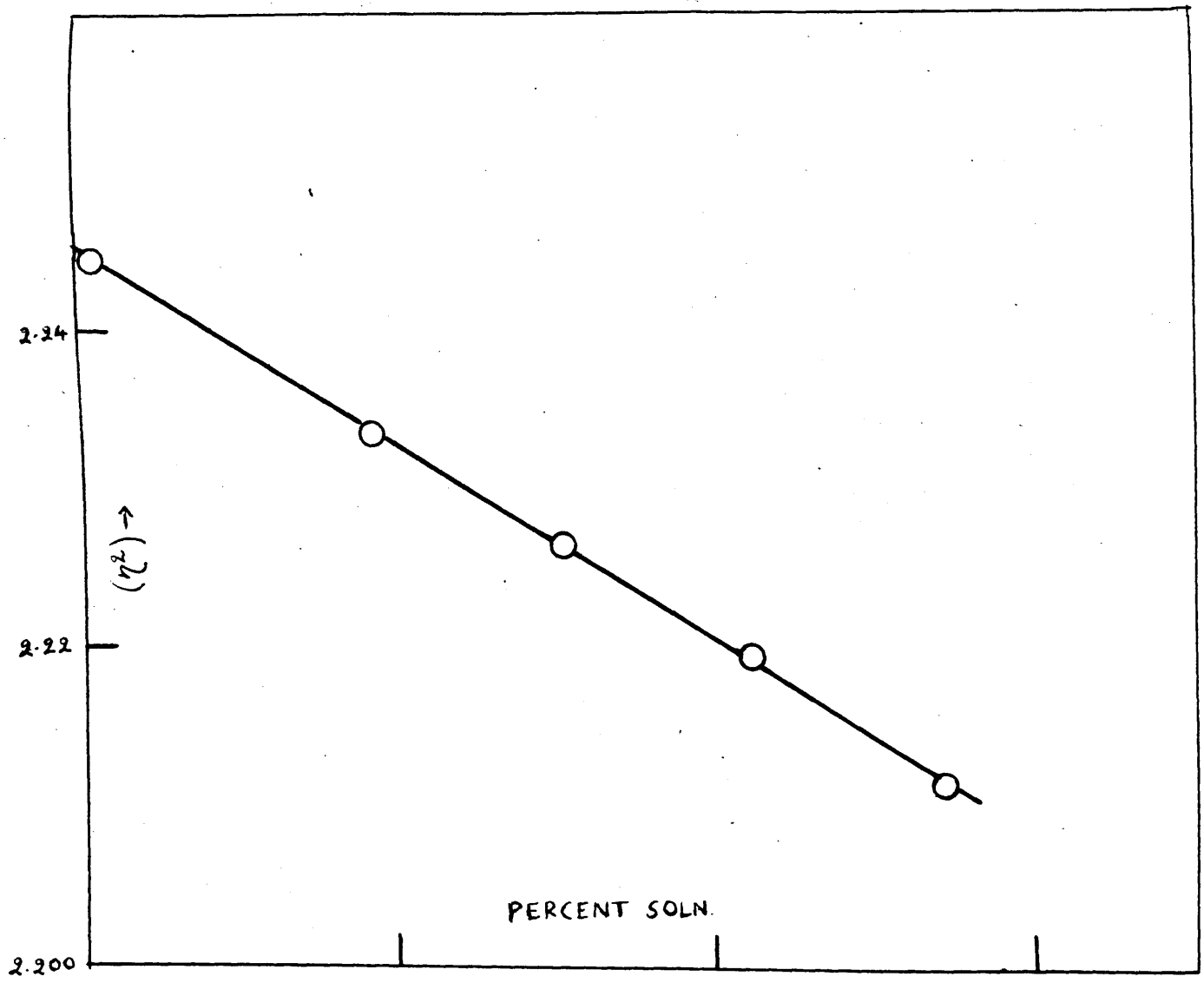

Fig. 5 CALIBRATION OF METHANOL IN BENZENE

η = refractive index

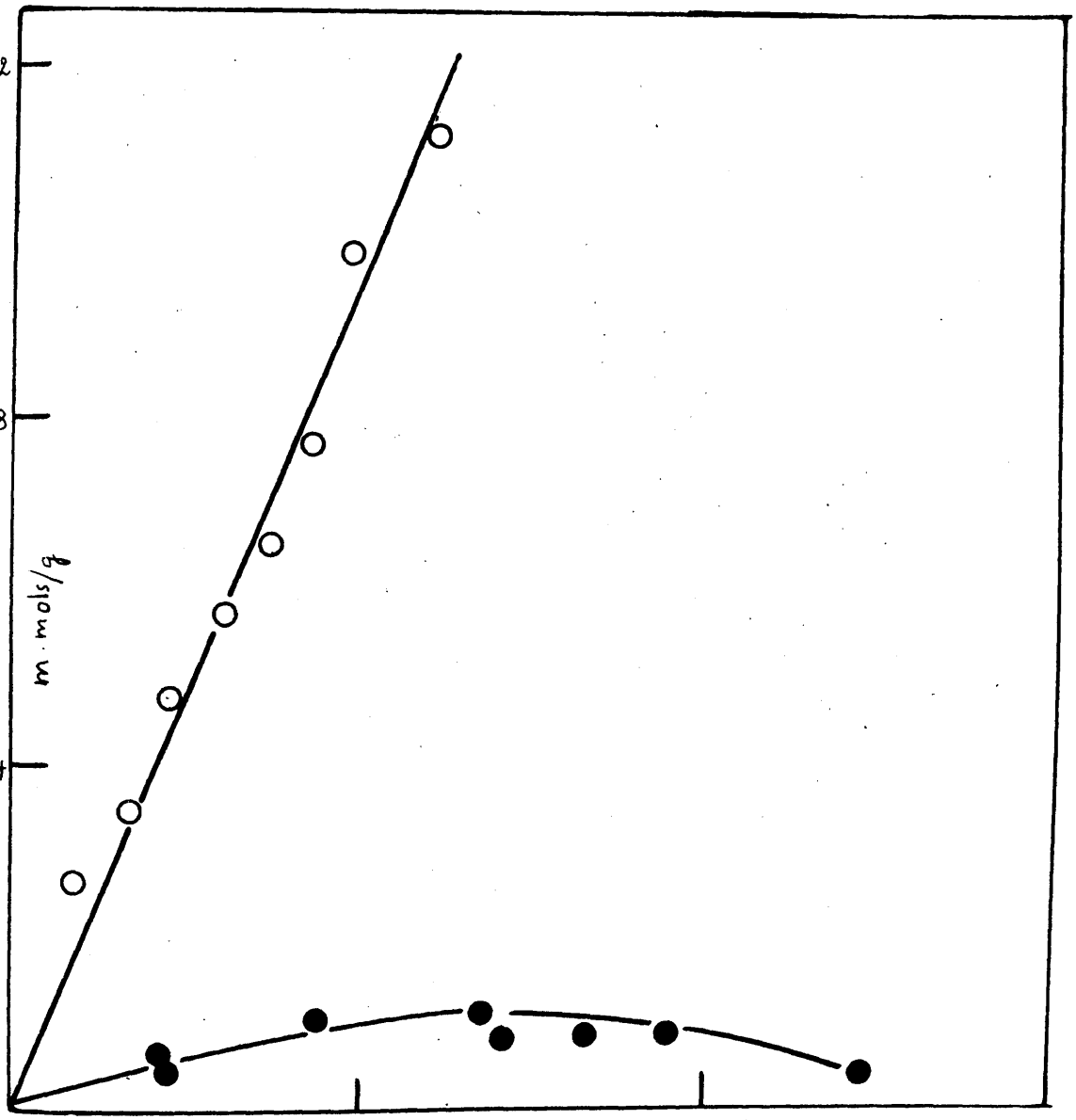

Fig 6 p-NO_2-PHENOL ON NYLON AND WOOL FROM BENZENE (60°)

1. NYLON
2. WOOL

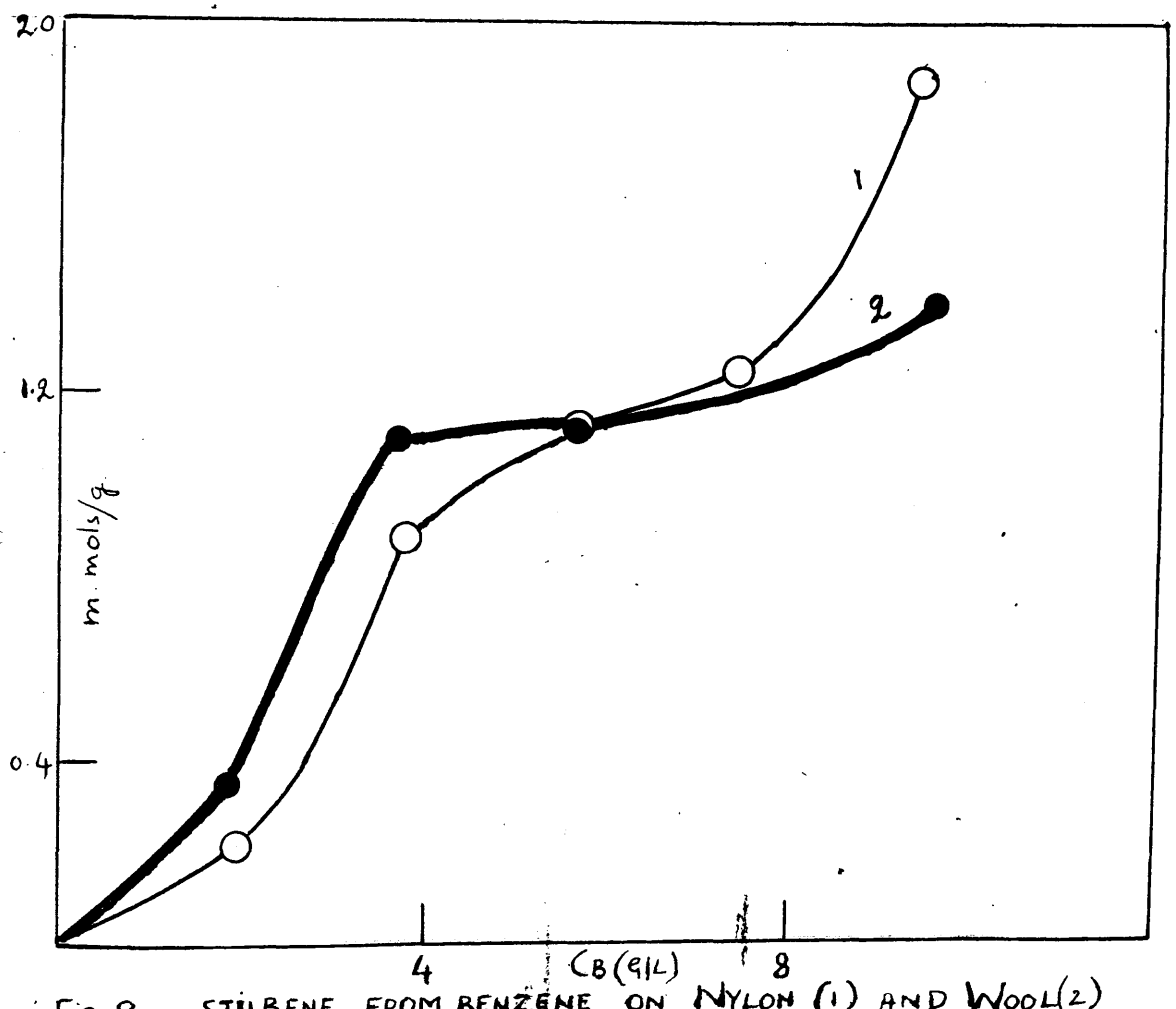

Fig 8 STILBENE FROM BENZENE ON NYLON (1) AND WOOL(2) AT 60°.

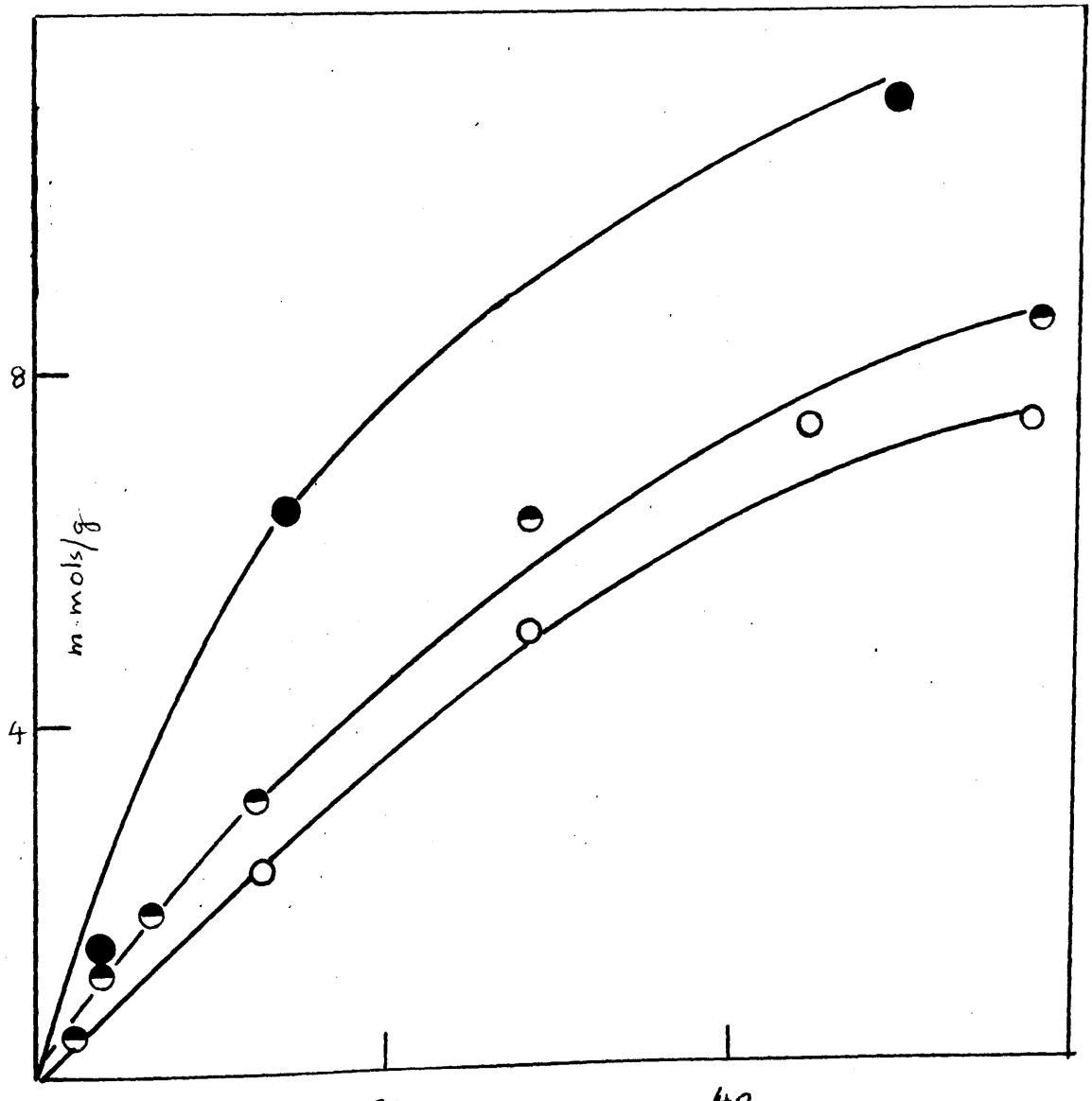

Fig 9. H_2O ON WOOL FROM n-BUTANOL

1. 30°
2. 52°
3. 57°

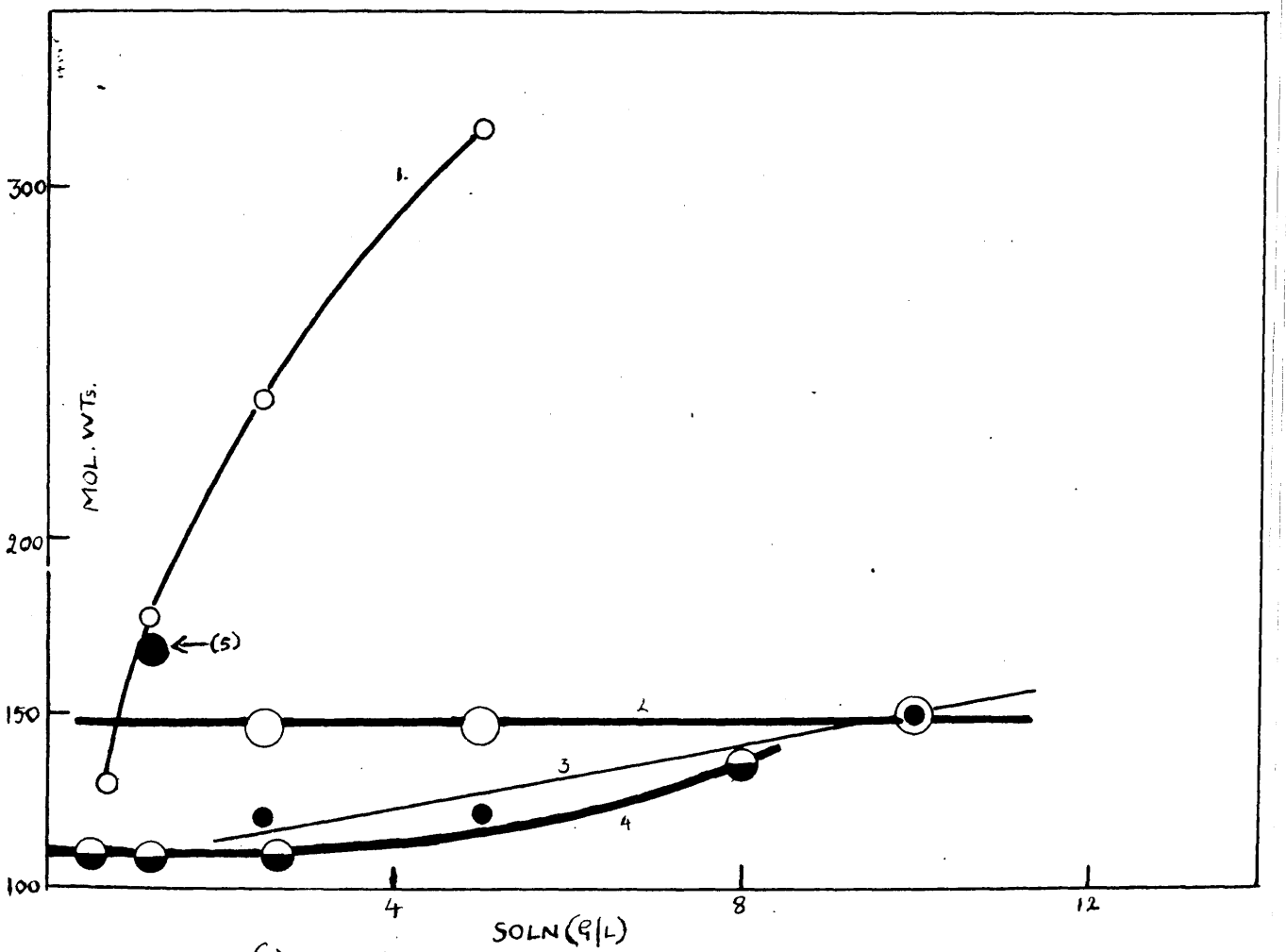

Fig. 10

1. p-OH-AZO-BENZENE (IN BENZENE)
2. β-NAPHTHOL "
3. α "
4. O-NITRO PHENOL "
5. DRIED SAMPLE OF (1) (100°) "

TABLE 1.

Summary of all the Sorption Experiments

Solvents: A = acetone; B = benzene; iBu = isobutanol Bu = n-butanol; C = carbon tetrachloride; mC = m-cresol; D = dioxan; E = diethyl ether; El = ethanol; EG = ethylene glycol; H = cyclohexane; M = methanol; O = isooctane; P = n-pentanol; iP = isopropanol; nP= n-propanol; T = toluene; W = water.

Substrates: N = nylon; Na = alkali-treated nylon; N_{69} = "6:9-polyamide"; S = silk; W = wool; Wa = alkali-treated wool; Wd = super-dry wool

Compound	Solvent	Substrate	Temp. (°C)	Time (h)	Result S = sorbed NS = not sorbed
Acetone	B	N, W	30	100	NS
	D	N, W	30	100	NS
	O	N, W	30	100	NS
	W	N, W	30	100	NS
p-Aminoazobenzene	B	W	30,50	100,50	S
Aniline	B	W	50	45	NS
	C	W	50	45	NS
Anthracene	B	N, W	35	60	S
Azobenzene	B	N, W, Wa	30-60	160-25	S
	mC	W	50	25	NS
	C	W			S
Azoxybenzene	B	N,Wd	60	24	NS
	C	Wd	60	24	NS
Benzene	Bu	W	50	24	S
Benzoic acid§§	W	N	25,40	15	S
Benzeneazo-α-naphthol	B	W	60	50	NS

Compound	Solvent	Substrate	Temp. (°C)	Time (h)	Result S = sorbed NS = not sorbed
Benzeneazo-ß-naphthol	B	N,N69,W,Wd	60	50	NS
	BE(1:1)	N, W	25	35	NS
	C	Wd	60	15	NS
Benzeneazo-m-toluidine	T	W, N	50,60	48	NS
Benzephenone	C	Wd	60	15	NS
	H	N, W	40	30	NS
	T	N, W	40	30	NS
Benzoquinone	D	N, W	35,60		NS(?)
Bis-phenylazo-benzene	B	N, W	50	50	NS
n-Butanol	B	N, W	50,30	50,75	NS
Catechol §§	W	N,S,W			S
Diethylamine	C	W, N	50	48	NS
	W	W, N	50	48	NS
N:N'-Dimethyl-4-aminoazobenzene	B	N,	60	25	NS
	C	Wd	60	25	NS
Diphenyl	B	N, W	60	60	NS
4'-Dodecylbenzeneazo-p-cresol	B, C	N,N69,Wd	60	25	NS
Haematoxylin	El	W	30	50	NS(?)
	§§W	N,S,W	30,60	70,25	S
2-Hydroxyanthraquinone	Bu	N, W	50	25	NS
	D	W	50	25	NS
	El	W	50	50	NS
o-Hydroxyazobenzene	B	W	30,50	100,70	S
p-Hydroxyazobenzene	B	N,N69,W,Wa	60	25	NS
	C	Wd	60	25	NS
	ElW(1:1)	Wd	60	25	NS

Compound	Solvent	Substrate	Temp. (°C)	Time (h)	Result S = sorbed NS = not sorbed
Water	BEl(4:1)	W	50	20	S
	Bu	N, W	30,52,57	90,50,25	S
	iBu	W	50	20	S
	D	W	50	20	S
	El	W	50	20	S
	M	W	25	70	S
	P	W	50	20	S
	iP	W	50	20	S
	nP	W	50	20	S

§§ Compounds reported previously

TABLE 2.

Sorption-isotherms of p-Aminoazobenzene from benzene on Wool at 30° 50°C (Na-dried solution) after 100 and 50 hours respectively.

Temp. 50°C		30°C	
C_B	C_F	C_B	C_F
1.35	0.083	1.35	0.083
3.15	0.11	3.6	-
5.0	0.13	5.35	0.083
9.7	0.038	8.6	0.18

TABLE 3.

Some earlier results of sorption of Azobenzene from benzene on Wool and Nylon (without Na-drying the solution). Hrs: 50

Temp: 60°C Fibre: Nylon		Temp: 60°C Fibre: Wool	
C_B	C_F	C_B	C_F
.0087	.00022	.033	.0015
.017	.0005	.047	.0029
.034	.00098	.083	.0037
.017	.00078	0.31	0.011
.035	.0011	0.48	0.015
.049	.0024	0.62	0.026
.066	.0031	0.77	0.042
..084	.003516	1.9	0.017
0.18	0.0033	5.0	0.17
0.36	0.0066	7.0	0.17
0.55	0.0082		
0.90	0.017		
1.9	0.017		
4.9	0.18		
6.9	0.18		

N.B. For all the tables including these above:

C_B = Equilibrium concentration of the bath in g/l

C_F = Sorption on the fibre m.mols/g. of fibre.

TABLE 4

Sorption-isotherms of Azobenzene from benzene on Wool and Nylon at 30°C and 50°C. (Na dried solution) after 160 and 50 hrs.resp.

Temp 50°C	Fibre Wool	Temp. 30°C	Fibre Wool
C_B	C_F	C_B	C_F
0.95	0.014	0.9	0.0275
1.7	0.082	1.65	0.096
3.32	0.187	3.25	0.21
5.2	0.22	5.10	0.25
7.0	0.275	6.8	0.33
Temp 50°C	Fibre: alkali treated wool	Temp. 50°C	Fibre:alkali treated nylon
0.78	0.061	0.9	0.0275
1.6	0.11	2.0	--
3.2	0.22	2.95	0.014
4.85	0.32	5.72	0.077
		7.8	0.061
		9.6	0.11
Temp. 50°C	Fibre: Nylon	Temp. 30°C	Fibre: Nylon
0.55	nil	0.9	0.028
1.7	nil	1.85	0.041
3.2	0.01	5.72	0.077
4.3	0.01		
5.3	0.02		

TABLE 5.

Sorption-isotherm of Benzene from n-butanol on Wool and Nylon at 50°C, 50 hours.

C_B	C_F	C_B	C_F
6.0	0.89	38.0	4.68
13.0	1.45	61.5	2.76
30.0	1.62	84.0	1.17

TABLE 6.

Sorption-isotherms of N:N-Dimethyl-4'-aminoazobenzene from benzene on Wool at 30 and 50°C after 160 and 50 hours respectively.

Temp. 30°C		Temp. 50°C	
C_B	C_F	C_B	C_F
0.9	0.022	1.0	nil
1.85	0.033	2.0	nil
7.70	0.067	3.9	0.022
9.65	0.078	5.85	0.033
		7.85	0.034
		9.40	0.13

TABLE 7.

Sorption-isotherms of Methanol from benzene on Nylon and Wool at 30°C and 50°C for 120 and 50 hours respectively.

Temp. 50°C C_B	Fibre: Wool C_F	Temp. 30°C C_B	Fibre: Wool C_F
3.0	2.283	2.5	2.674
7.0	3.784	2.8	7.07
15.5	6.80	12.0	9.135
28.5	5.50	25.0	10.32
39.5	4.923	33.7	10.68
51.5	4.83	45.0	11.11
Temp. 50°C C_B	Fibre:Nylon C_F	Temp. 30°C C_B	Fibre:Nylon C_F
1.0	3.846	0	9.251
10.0	10.69	10.5	10.30
21.0	11.36		
39.5	6.172	32.5	11.62
47.5	9.16		

TABLE 8

Calibration of Methanol in benzene by refractometric method (Abbe)

No	Concn(g/l)	η^2(24°C) (η = refractive index)
1	5.922	2.24415
2	11.844	2.24155
3	13.688	2.23305
4	35.532	2.22605
5	47.376	2.21905
6	59.220	2.21135

TABLE 9.

Sorption of p-Nitrophenol on wool from 10 g./l solutions in Different Solvents.

Time (hrs)	Amount Sorbed (m.mols/g.) Benzene 40°C	B.P.	Ethanol 40°C	B.P.	Isooctane B.P.	Dioxan 40°C
2			0.04			
6		nil	-	0.16	nil	oxidative effects
18	0.033		0.10			prevent measure-
24	0.066		0.36			ment by 'Spekker'
96	0.166		0.336			photometer

TABLE 10

Sorption isotherms of p-Nitrophenol from benzene on Wool and Nylon at 60°C for 25 hours.

Fibre: Nylon		Fibre: Wool	
C_B	C_F	C_B	C_F
0.71	0.28	1.7	0.065
1.38	0.350	3.5	0.108
1.77	0.481	5.65	0.0755
2.35	0.572	7.60	0.0862
2.95	0.66	9.80	0.0431
3.4	0.777		
3.85	0.902		
4.80	1.22		

TABLE 11.

Sorption-isotherms of Phenol from water on Nylon and Wool at 30°C and 50°C for 70 and 50 hrs. resp.

Temp: 30°C Fibre: Wool		Temp. 50°C Fibre: Wool	
C_B	C_F	C_B	C_F
1.57	0.2027	1.78	0.0923
3.26	0.3474	3.343	0.3021
6.714	0.5224	6.785	0,4846
13.78	-	12.52	(0.33)?
16.21	1.436	16.81	1.117
Temp: 60°C (20hrs) Fibre:Nylon		Temp.30°C	Fibre: Nylon
C_B	C_F	C_B	C_F
1.042	0.2411	2.184	0.4592
3.783	0.4203	3.211	0.5453
8,706	0.9371	4.508	0.8478
13.14	0.9908		
18.91	1.745		

TABLE 12.

Sorption-isotherms of Phenol from ethanol on Wool at 40°C and 50°C for 50 hrs. each

Temp: 40°C		Temp: 50°C	
C_B	C_F	C_B	C_F
1.99	nil	2.087	0.0039
3.9	nil	7.633	0.0510
6.621	0.6649	15.02	0.093
11.36	2.30	16.60	0.275
12.77	3.67		

TABLE 13

Sorption-isotherms of phenol from isooctane on Wool, Cotton (and Viscose)

Wool and viscose showed no sorption at 50°C even after 48 hrs.

Temp: 50°C. Fibre: Cotton (surgical)		Temp 30°C hrs. 65	Fibre: Wool
C_B	C_F	C_B	C_F
0.16	0.0213	0.155	0.024
0.345	0.03	0.345	0.030
0.745	0.03	0.705	0.051
1.465	0.072	1.475	0.066
1.750	0.130	1.775	0.12

N.B. At B.P. both ethanol and isooctane gave no sorption on wool

TABLE 14.

Sorption-isotherms of Stilbene from benzene on Wool and Nylon at 60°C for 25 hrs.

Fibre: Wool		Fibre: Nylon	
C_B	C_F	C_B	C_F
1.87	0.0357	1.92	0.022
3.6	0.11	3.68	0.088
5.6	0.11	5.6	0.11
7.7	0.0824	7.55	0.1236
9.5	0.1374	9.32	0.187

TABLE 15

Sorption-isotherms of Water from n-butanol on Wool at 30°C, 52°C, 57°C for 90, 50, 25 hrs. resp.

Temp: 57°C		Temp: 52°C		Temp: 30°C	
C_B	C_F	C_B	C_F	C_B	C_F
5.856	1.933	2.239	0.3945	4.448	1.469
11.85	2.361	3.429	1.190	16.52	6.472
28.18	5.05	6.380	1.852	53.67	11.0
44.57	7.389	12.38	3.166		
57114	7.389	14.47	2.667		
		28.18	6.360		
		57.90	8.478		

TABLE 16

Sorption of water (4.996 g./l.) from Different Solvents at 50°C 18 hrs.

Solvent	Sorption m.mols/g.
Dioxan	1.110
n-Propyl-alcohol	1.267
iso-Propyl-alcohol	(0.5833)
n-Butyl alcohol	0.9731
iso-Butyl alcohol	1.423
n-Amyl alcohol	1.783
Benzene/Ethanol (4:1)	2.9
Ethanol and Methanol show no sorption	

TABLE 17

Sorption-Isotherm of Hydroquinone from water on Nylon and Wool at 37°C, 40 hrs.

Fibre: Nylon		Fibre: Wool	
C_B	C_F	C_B	C_F
2.987	0.2081	3.430	0.087
6.063	0.3918	11.07	1.072
13.28	0.4690		

(This experiment was done just to test the previously reported experiment and was found to agree with it very well)

TABLE 18

List of compounds sorbed only in traces from dilute solutions on Wool and Nylon.

				Wool		Nylon	
Compound	Solvent	Temp. °C	Hrs.	C_B	C_F	C_B	C_F
Anthracene	Benzene	37	70	1.8	0.038	1.8	0.038
				3.8	0.038		
ß-Naphthol	"	50	70	3.8	0.072		
p-Hydroxyazo benzene	"	50	70	0.034	.0009		

In the case of the first two compounds higher concentrations showed no sorption (from the 'Spekker' photometer readings) while the third compound was not available in large quantities to do more tests.

TABLE 19

Solubility of Nylon in Different Compounds at their M.P.s

Compound	Results
p-Hydroxyazobenzene	Soluble
p-Nitrophenol	Soluble
NN'-Dimethyl-4-aminoazobenzene	Less soluble
Benzene-azo- _ -naphthol	Less soluble
Hydroquinone	Very easily soluble
Resorcinol	Very easily soluble
2:3:4 Trihydroxybenzophenone	Soluble
Catechol	Soluble
2:4 di-Nitrophenol	Soluble
p-Aminoazobenzene	Less soluble
o-Nitrophenol	Not soluble
Azobenzene	Not soluble
Benzeneazo-ß-naphthol	Not very insoluble
Azoxybenzene	Not soluble
Phenylhydrazine	Not soluble
p-methoxy-azobenzene	Not soluble
2:4 di-Nitroaniline	Not very insoluble

REFERENCES

Arshid and Giles, unpublished work.

Astbury, J.Soc.Chem.Ind., 1930, 49, 441.

Astbury and Dawson, J.S.D.C., 1938, 54, 6.

Barr and Speakman, J.T.I., 1944, 35, T 77.

Bartell et al, J.Phys.Chem., 1952, 56, 665.

Bath and Ellis, J.Chem.Phys., 1941, 45, 204.

Buswell, Rodebusch and Roy, J.A.C.S., 1938, 60, 2444

Boulton, J.S.D.C., 1946, 62, 65.

Burnbaum, Linford and Style, Trans.Faraday.Soc., 1953, 49, 735.

Burns and Garner, Proc.Roy.Soc., 1941, 63, 2828.

Cassie, S.D.C. Symposium, 1946, p.86.

Davies, Chem.Soc.Ann.Reports, 1946, 43, 5.

Dole and McLaren, J.A.C.S., 1947, 69, 651.

Edsall, J.Polymer Sci., 1954, 12, 253.

Elöd and Zahn, Melliand Textilber, 1948, 29, 17.

Flett, J.S.D.C., 1952, 68, 59.

Gilbert and Rideal, Proc.Roy.Soc., 1944, A 182, 335.

Gralén, J.S.D.C., 1950, 66, 465.

Gustavsen, J.Polymer Sci., 1954, 12, 317.

Harkins and Gass, J.A.C.S., 1931, 53, 2804.

Haurowitz, "Chemistry and Biology of Proteins" Academic Press Inc. N.Y. U.S.A., 1950, p.32.

Howitt, "Fibre Science", ed:Preston. The Textile Institute.1949

King, Trans.Faraday Soc., 1940, 36, 335:
ibid., 1945, 45, 35;
ibid., 1947, 2, 551.

Lindberg, Text.Res.J., 1953, 23, 67, 225, 573, 585.

Lloyd and Garrod, S.D.C. Symposium, 1946, p.24.

Magne and Skau, Text.Res.J., 1952, 22, 748.

Marsden, "Fibre Science" Ed. Preston, Manchester, 1949,p.181.

Marsden and Urquhart, J.T.I., 1942, 33, T 105:
ibid., 1944, 35, T 77.

Mehta, Ph.D. Thesis, Glasgow University, 1950.

Meredith, "Fibre Science" p.193.

Oxflogsen, J.Polymer Sci., 1953, 12, 301.

Parkshver, Mankesh and Kukanova, Textil.Prom., 1951(June), 11, 15. Through J.S.D.C., 1951, 67, 473.

Pauling et al., Proc.Nat.Acad.Sci., 1951, 37, 205, 235, 251, 256, 261, 272, 282.

Peters, S.D.C. Symposium, 1946.

Robinson and Ambrose, Trans.Faraday Soc., 1952, 48, 854.

Sookne and Harris, J.Res.Nat.Bur.Standards, 1939, 23, 299.

Speakman, J.S.D.C., 1933, 44, 180.

Speakman and Stott, Trans.Faraday Soc., 1935, 31, 1425
ibid., 1938, 34, 1203.

Steinhardt and Harris, J.Res.Nat.Bur. 1940, 24, 335.

Steinhardt, Fuggit and Harris, ibid., 1941, 26, 293.
ibid., 1940, 25, 519.

Takenhiko et al, Science, Japan, 1943, 13, 29.

Traill, J.S.D.C., 1951, 67, 257.

Tsuboi, Bull.Soc.Chem. Japan, 1952, 25, 60.

Vickerstaff, J.S.D.C., 1943, 49, 92: ibid., 1953, 69, 279.
Also "Physical Chemistry of Dyeing" 1950 Chap.10-12

Vickerstaff et al, J.S.D.C., 1945, 61, 193: ibid, 1947, 63, 388.

Wilkinson and Tylor, J.S.D.C., 1928, 44, 369.
Walker: Fibres from Synthetic Polymers Ed.R.Hill,Elsievier,1953

§§§§§§§§§§

PART II

MECHANISM OF DYE SORPTION ON WOOL AND NYLON.

(Sorption at organic interface .)

(B) Vapour Phase

SUMMARY

The effects of various treatments applied to wool fibres, e.g. drying under different conditions, dyeing with acid wool dyes, etc.,upon the rates of sorption thereon of methanol vapour have been studied over a range of pressures and temperatures. Measurements of heats of sorption suggest that a hydrogen bond is formed between methanol and the protein molecules in the fibre.

INTRODUCTION

Almost all published work upon vapour phase sorption on textile fibres is concerned with the sorption of water vapour, for on this there depend a number of fundamental properties of such materials, e.g. strength, extensibility, wettability, dyeing properties etc. Besides, if the mode of attachment of water molecule to fibre is known, it provides a very useful clue to the internal structure of ~~the~~ the fibre. Shepperd and Newsome studied the affinity of water vapour for cellulose and so did Urquhart and Williams; whilst proteins, including protein fibres and nylon, have been investigated by Bull, who explained the structure of the solid proteins as consisting of coherent planes linked together, the exposed surfaces being highly hydrophilic. Extensive surveys of sorption of water vapour by textiles in general, and proteins, have been made by Carlene and by MacLaren and Rowen respectively. It is evident from these surveys that no unified theory can possibly explain the entire range of sorption. The isotherms of Pierce and Cassie, for example, assumed that sorbed water molecules in the second and successive stages are in the free state (Gilbert, however, strongly questions this assumption). Recently Cassie has explained water sorption at high regains on the basis of entropy increase, thus accounting for the decrease in the heat content of the system. He also calculated the 'work' of

swelling and heat of sorption of the stress-free isotherm, as 6.6 kcals/mol. Hailwood and Horrobin, on the other hand, consider the sorbed water as an ideal solid solution composed of dissolved, chemically bonded and hydrated water. Their data on heat calculations agree with those of Bull (loc.cit.). Recently Larose has studied the effect of acid dyes on wool on its sorption capacity for water vapour. His results seem to identify the free amino groups in wool as the specific sites of sorption for water molecules.

There is very little data on other vapours. Kanamaru and Chao and Lauter studied a number of organic vapours on cellulosic materials. King studied the rates of vapour sorption of water, methanol and ethanol on wool and considered that the diffusion rate rather than the molecular size is the controlling factor in such sorptions; the slow dissipation of the heat evolved retarding the process. He actually measured the rise in temperature of the fibre during sorption. Later he also studied some strongly hydrogen bonding agents, e.g. water and formic acid on wool and nylon and showed that the increase in dielectric constant of the sorbent after sorption was not dependent on the dipole moment of the sorbate but was correlated with the decrease in the elastic modulus.

The previously reported work carried out in this laboratory (V.B.Chipalkatti, Ph.D. Thesis, Glasgow University, 1950) on nylon and wool consisted of a sorption study of a number of hydroxylic compounds from the vapour phase, e.g.

water, methanol, ethanol, phenol, α and β-naphthols etc. He considered that these substances are probably sorbed on the fibres through hydrogen bonding. The results of the studies from the liquid phase (c.f. Part II A) are in agreement with this view, with certain limitations. In order to elaborate this point the present work was undertaken, particularly to compare the liquid phase sorption studies (from dry non-polar solvents) with vapour phase sorption. Methanol, which has a conveniently measurable sorption rate on nylon (V.B.Chipalkatti) was selected for the purpose of sorption studies on wool.

EXPERIMENTAL

The Sorption Apparatus.

The McBain and Bakr spring balance method was used in the assembly shown in Fig. 17 which represents the design latterly used. The reagent was contained in a thin sealed glass capsule in the Tube A and was released by dropping on to it a stainless steel ball-bearing, which was raised by a magnet. The apparatus was evacuated to 10^{-4} m.m. of Hg pressure (measured by McLeod gauge). It was found that this material gave very satisfactory results, provided the spring was heated under (maximum) load at 200°C. for about 12 hrs. before use to ensure dimensional stability (Giles and V.B.Chipalkatti). The dimensions of a typical spring are: fibre diameter 0.008 in.; coil diameter 0.75 in.; turns per in. 12; sensitivity 17.5 cm. per g. with a 0.4 g. load. The extension was measured to 0.0001 cm. by a cathetometer.

For the low temperature experiments ($< 40^{\circ}$C.) the whole apparatus was enclosed in an air thermostat constructed on the table of the vacuum unit (two stage Barr and Stroud lens coating unit). For high temperature the apparatus was modified as per Fig. 18 and was found to work satisfactorily. The bath was constructed of copper with a Pyrex plate glass window through which the spring was observed. The oil was circulated by a pump. The sorption tube was immersed in a thermostatically controlled bath of paraffin

oil. The reagent reservoir was outside in closest possible proximity. Thus the reagent, if very non-volatile, could be independently heated to a slightly higher temperature than the bath. (No high temperature work has been reported here).

In order to avoid condensation of liquid from entering vapour after expansion into the sorption tube, the vapour was first allowed to remain in the vapour reservoir a short time before slowly letting it into the sorption tube, the walls of which had been very slightly warmed by a brief application of a luminous gas flame. Without these precautions, the spring registers an initial rapid increase of weight of the substrate on the impact of the vapour, followed by a slight decrease and then the normal steady rise.

Degassing treatment:

All the fibre samples in each series of tests were degassed at 10^{-4} m.m. Hg pressure at the temperature of the experiment, and for the same length of time, before sorption was commenced. Practical difficulties limited the normal de-gassing period to 4-5 hours, but a few experiments, with longer periods of degassing, appear to show that 4-5 hours may not be sufficiently long for complete removal of all traces of residual vapour. This point is illustrated by the data of Tables 1 and 2. These results would appear to show not only that very considerable de-gassing periods might be

required for complete removal of all traces of sorbed vapours, but that the firmly-held traces of vapour not removed by degassing are capable of blocking the internal fibre structure in some manner which prevents the entry of a much larger amount of fresh vapour in the sorption test.

In view of practical difficulties in performing the longer degassing treatments, and the apparent good reproducibility of the results of the shorter treatments, it was then decided to standardise the period of 4-5 hours for the present work.

Quite often, the earlier investigators have determined isotherms in vapour phase studies by repeated sorption and desorption treatments upon single samples of sorbent (particularly with a view to studying hysteresis phenomena). In view of the demonstration in this work that such a procedure can lead to considerable structural changes, it was considered undesirable to follow this practice with fibres. Accordingly, all the isotherms have been determined from series of fresh fibre samples. This makes the determination of isotherms a somewhat long and tedious process, and few have therefore been determined.

Materials:

The fibres and the other materials were identical with those used in Part II A.

Deamination of wool:

This was done by treating wool with Van Slyke's reagent (Speakman, J.T.I., 1947, 38, T 102) e.g. 7 ml. of glacial acetic acid was added to 30 ml. of 30% (w/v) sodium nitrite and 20 ml. of this solution was added to each g. of wool. The fibre was immersed for 48 hours at room temperature and then washed in running water for 8-10 hours. After leaving overnight in distilled water, and being rinsed again, the fibre was dried at 60°C. and conditioned to room temperature for 48 hours.

Dyed wool:

Three samples were prepared as follows:

(a) dyed to saturation using Solway Blue BNS (C.I.No.1054) - a levelling acid dye, at pH 1-2 by Vickerstaff and Skinner's method (J.S.D.C., 1945, 61, 193), excess acid being removed by washing;

(b) dyed with about 10% of its weight of Coomassie Navy Blue GS (C.I.No.289) - a milling acid dye - at neutral pH, the dye having been purified by passing through an ion-exchange resin column (purity by Titanous Chloride method - 90%);

(c) dyed with Azo Geranine 2GS (C.I.No.31) to saturation (0.006 g. per g. wool) under neutral conditions.

Method of specially drying wool to remove the last traces of moisture:

(a) A sample of wool was soaked in methanol, then in "Specially dried" methanol, 12 hrs. each (in a Quickfit tube with tight stopper) and then dried directly by degassing;

(b) as (a) but ether (dry) was used as final soaking agent and removed during degassing;

(c) as (a) except that benzene (dry) was the final soaking agent, being removed at the degassing stage;

(d) after treatment as in (a), the sample was soaked in glacial acetic acid and finally in anetic anhydride, the latter being removed during degassing;

(e) after treatment as in (b), isopropyl alcohol was used as the final soaking agent, followed by degassing under vacuum as before.

Sorption rates:

These were obtained from the slopes of the plot

$$t \text{ vs } \log \left\{ \frac{C_E}{C_E - C_F} \right\}.$$

t = time in min.

C_E = Equilibrium Sorption (m.mols./g. of fibre).

C_F = Sorption at any time (t) during sorption (m.mols./g.)

RESULTS AND DISCUSSION

Effect of Sorption-desorption cycles.

Tables 1 and 2 give some of the preliminary experiments to ascertain the effects of sorption-desorption cycles on a single sample of fibre. It is evident in nylon that each such cycle raises the rate of sorption and equilibrium value of the subsequent sorption though the effect is not so well pronounced as it is for phenol or β-naphthol vapours (V.B. Chipalkatti). Desorption, on the other hand, becomes more and more difficult, thus showing there is an increase of available area after every such cycle of sorption and desorption.

The effects on wool are not so well defined. Overnight degassing (as against the normal 4 to 5 hours) produces much enhanced sorption, which was not evident in nylon. Also, a sudden rise in sorption rate, at about 1 to 1.2 m.mol./g. indicates there are two types of sorption involved (see Table 2, Figs. 1, 2, 3, 4). Thus the firmly bound moisture (or other vapour) is capable of 'blocking' the fibre and affecting sorption rates on wool in some permanent manner, since samples left for 4/5 days after sorption-desorption cycle do not seem to give very consistent results. (Table 2, Samples III).

The first order law of rates is fairly well obeyed (see Figs. 2, 4, 5, 7, 9) even though the initial time lag seems

to vary from sample to sample (from the same lot of wool); and this again diminishes during the sorption-desorption treatment. It is probably the epicuticle (acting simply as a mechanical barrier) that is responsible for such phenomena, for in some experiments in the liquid-phase threshold-concentrations, below which no sorption occurs, were noticed particularly with dry solvents.

In all the subsequent work, each experiment was made with an individual sample of wool chosen from the same lot.

Sorption Rates:

Experiments at 27°C. In order to test the reproducibility of rates (to which reference has already been made), a series of replicate experiments was carried out (at 40 m.m.) and the results plotted in the form of first order constants. The linearity of the plot is quite reasonable considering possible sample to sample variations (Fig.5). Much better reproducibility is obtained at higher pressures (see Fig. 2, 7, 4.). At this temperature and at low pressures the rates of sorption are sometimes too low and hence extrapolation from the ordinary rate curve was performed whenever necessary, as shown in the Table 2. On the other hand at higher pressures equilibrium is reached rather rapidly and the sorption values very near to the equilibrium value tended to deviate from the line drawn from the first order constants. But in general the first order constants gave consistent and

orderly results whose relationship with the vapour pressure of methanol is shown in Fig.8. The rate of change of slope of the first order rate with vapour pressure is indicative of two types of sorption being involved, e.g. one up to ca 98 m.m. and the other above that pressure.

The equilibrium sorption value in this region of transition is about 4 to 4.5 m.mols per g. of wool. This is very near the value quoted by Bull and also by McLaren and Rowen, for the monolayer formation of water vapour on wool. Thus methanol sorption on wool under these conditions seems to be identical with that of water, which has also been pointed out by V.B.Chipalkatti as a result of his experiments on nylon. (See also isotherms study). If this is so, methanol, like water, attaches itself to the polar side chains of wool by hydrogen bonding. Similar results were also obtained in the liquid phase (e.g. water from n-butanol Part II A) but they were not so well defined and hence have not been quoted here. This view is supported by the fact that methanol is tenaciously held even after prolonged degassing.

Experiments at 40°C: The reproducibility of the sorption rates (i.e. slopes of the line from first order constants) is much improved at this temperature (see Fig. 9) even in the lower vapour pressure region, but the irregularity of the points near to the equilibrium value is still

noticeable. This is to be expected, from the increased rate of sorption. The overall relationship of the rates to the vapour pressure of methanol is different from the previous one, e.g., there is a much more gradual change in the initial part of the curve, while the transition point is shifted to an equilibrium sorption value corresponding to ca. 2.5 m.mols./g. This must mean that the monolayer capacity has become reduced to a little more than half the value in the previous experiment. This implies that the reaction is exothermic, since the vapour pressure is of the same order as before.

Isotherms at 27°C and 40°C. Fig. 11 shows the ordinary isotherms of methanol vapour on wool at these temperatures. The apparent heat of sorption calculated from these is ca. 4 to 5 kcal. per mol., which is of the correct order for a OH.....O bond, thus confirming the view previously expressed (Part II A) upon its nature. This value remains constant down to zero sorption, provided the curves are extrapolated back as shown by the dotted lines. This is on the assumption that the anomalous values at the lower end of the 27 C.° curve are fictitious, and due solely to a very low rate of sorption having prevented the attainment of true equilibrium. If these values are true then the heat of sorption in the lower region would be so low as only to be accounted for by van der Waals attraction. In that case it would be necessary

to assume that the first layer of molecules are physically adsorbed, but as the amount of methanol sorbed increases, more and more molecules become attached to the fibre by hydrogen bonds, presumably by association with the previously adsorbed molecules.

The application of the BET equation gives the following constants (see Fig.12)

Temp. (^{o}C)	C_m (m.mols/g.)	C	$E_1 - E_L$	E_1 (cals/mol.)
27	1.681	6.841	1142	9592
40	1.806	5.340	1037	9487

where C_m = monolayer capacity

$C = e^{E_1 - E_L/RT}$

E_1 = heat of sorption

E_L = heat of condensation

R = gas constant (1.98 cals/mol.)

T = absolute temperature.

Here again the first two points at $27^{o}C$ do not lie on the straight line in Fig.12 for reasons already given. The heat values are rather high but are of the same order as for methanol and phenol vapours on nylon (V.B.Chipalkatti), which suggests an identicity of the sites involved in all these cases and the mechanism of bonding. The latter cannot be of van der Waals

type, both from a consideration of the magnitude of the heat evolved and the size of the molecules. The values are of the same order as obtained by Dole and MacLaren for water vapour on nylon .

The monolayer capacity, however, does not agree with that obtained from rate considerations. It seems to be higher than would correspond to the free amino groups in wool (e.g. 0.082 m.equivalents per g.), thus these free amino groups themselves are of no particular significance, and this is further corroborated by experiments on dyed wool (see later).

Isotherms drawn on the relative vapour pressure basis show entirely different phenomenon e.g. (Fig.16), the isotherm at 27°C is mainly below that of 40°C. Reasons for this may be:

(i) equilibrium is not reached; or

(ii) degassing is not complete; or

(iii) the epicuticle at low temperatures acts as a strong barrier.

These points are now discussed.

From the nature of the curves (Fig. 1, 3, 6) it is improbable that the true equilibrium values are much higher than these. The apparent equilibrium reached seems to be due to incomplete degassing of moisture at this temperature. Also the epicuticle might act as a mechanical barrier requiring a certain minimum threshold pressure before it can be broken

through.

Thus the two isotherms show a quite distinct characteristic for wool under two different conditions. The heats of sorption calculated independently from the BET equation are of the same order and the monolayer capacity is also of the same order, Thus the sorption is probably due to hydrogen bonding (OH.....O type), but in the first case (27°C.), the firmly-bound water is acting as a barrier, masking sorption sites to which methanol might become attached. Thus both the vapours must be concerned with similar sorption sites.

Fig. 13, 14 show the application of the Langmuir isotherm equation to the present case. Sorption above ca. 1.25 to 1.54 m.mols./g. is different in nature from that ~~above~~ below this region. This value is presumably identifiable with the monolayer capacity of wool, the low energy sites being rapidly filled and subsequent sorption taking place either on the secondary sites produced as a result of swelling of the fibre or on the previously sorbed molecular layer. This figure is not far from that calculated on the BET principles. The Langmuir theory, which disregards the interaction of molecules and assumes all the sites are identical is inapplicable here. Gilbert has pointed out that even in a single unimolecular layer, the magnitude of the lateral interaction determines whether the isotherm has a shape of the Langmuir type, or is sigmoid, or even shows a sharp break, corresponding to the presence of two phases(Fowler and Guggenheim,

Statistical Thermodynamics. Cambridge Univ.Press, 1939, p.429). Actually the true representative isotherm (e.g. 40°C. Fig.14) is of a sigmoid type or S-shaped from about 1. to 1.5 m.mols per g. while below it, it corresponds to type I of Brunauer's classification. Thus the general mechanism of methanol vapour sorption on wool seems to consist of the following stages:

(i) preliminary sorption on polar side chains to form a monolayer e.g., up to 0.1 to 0.2 relative vapour pressure (Langmuir region);

(ii) later sorption in one or more layers, presumably through a similar mechanism, in the region from 0.2 to 0.8 relative vapour pressure (BET region);

(iii) finally, sorption involving condensation of the vapour, beyond a relative vapour pressure of about 0.8

Sorption of Methanol Vapour on Dyed and Deaminated Wool

During an X-ray examination of variously treated fibres Astbury and Dawson observed that fibres dyed with Solway Blue (C.I.No.1053 and 1054 respectively) showed the presence of free dye crystallites oriented roughly along the length of the fibres. No evidence of crystallites was found in the case of Orange II (C.I.No.151) and Coomassie Navy Blue 2RN (C.I.No. 289).

Some evidence has recently been obtained in the course of studies of the photodegradation of dyes in fibres and

films (see Part I, also Macaulay, Ph.D. Thesis, Glasgow, 1954) suggesting that dyes may always be present in dry dyed fibres partly, if not wholly, as discrete aggregates or crystals.

The results presented in Table 3 seem to be consistent with this view, for Solway Blue B, which has been shown to be present in discrete crystals along the length of the fibre does show in three out of four cases some inconsistent reduction in sorption values, even though all the fibres were dyed under identical conditions. This inconsistency may therefore be due more to physical than chemical causes.

Azo Geranine 2GS (C.I.No.31) which has very low affinity for wool in a neutral bath, fails to show any specific effects, perhaps because its aggregates are too small. On the other hand Coomassie Navy Blue GS, a milling acid dye, with high affinity in a neutral bath, shows a similar discrepancy, e.g., a heavily dyed sample shows reduction in sorption value of methanol. This dye is known to form molecular aggregates and to combine with wool in large excess of its acid binding capacity.

Deaminated wool shows no difference, while the results of phenol treated samples are of doubtful character, since phenol at such drastic degassing (10^{-4}m.m./27°C. for 4 to 5 hrs.) would have desorbed. Besides it is known to occupy the same sites as methanol.

It has also been shown previously (V.B.Chipalkatti),

that sorption of water vapour on dyed (Solway Blue BNS) deaminated and acid treated wool was identical with ordinary wool while that of acetic acid vapour is reduced on dyeing. These results together with those discussed above may well be interpreted as that methanol or an even bigger molecule like acetic acid is incapable of negotiating the intermicellar pores due to the blockage of them by solid dye aggregates. In fact, recently published data by Larose of water vapour on dyed wool (Orange II) and those presented here fail to show rigorous stoichiometric relationship in reduction values and hence are in conformity with the view that these reductions are caused mainly by the incidental physical causes of particle growth of the dye in the amorphous material of the fibre.

Sorption of Methanol Vapour on Wool dried by various means.

Fig. 15 Table 6 . Isopropyl alcohol gives the highest sorption rate and methanol the highest sorption equilibrium value, at 40°C. and saturated vapour pressure. iso-Propanol, according to Speakman's estimate of pore size, should enter the intermicellar pores and swell them, but it cannot be very easily desorbed on account of its high boiling point, while at the same time it would occupy the same sites as the incoming methanol. In the case of methanol it is one of those effects equivalent to the sorption-desorption cycle already discussed. Benzene, which has been shown to be sorbed by van der Waals

forces (Part II A) does seem to offer mechanical resistance for further sorption of methanol as it may have also not been completely desorbed (c.f. dye crystallites in the preceding Part). Ether can be removed very easily, thus, probably it would be a good drying agent in the way used here since it has increased the sorption rate considerably (but not the sorption value which might be due to its incapacity to swell the wool). This observation is also consistent with the weakly bonding character of ethereal oxygen noted in Part II A.

Sorption of Miscellaneous Vapours on Wool at 40°C. and Saturated Vapour Pressure.

Table 7. Pyridine is not sorbed, benzene is sorbed, but only to a small extent. (Pyridine was not sorbed from the liquid phase, Part II A.). Benzene, which is sorbed from the liquid phase (e.g. from n-butanol) is sorbed in the vapour phase but to a lesser extent. Dioxan is sorbed in considerable amount, which might perhaps explain some of the negative results of sorption in the previous Part. n-Propyl alcohol is sorbed much less than methanol at the same temperature and pressure. Ethanol is sorbed slower than methanol (V.B. Chipalkatti) and the latter slower than water, on nylon. Thus molecular size seems to govern the rate of sorption, which has been often noticed in the liquid phase experiments, (Part II A).

CONCLUSIONS

The following general conclusions may be drawn.

i) Methanol combines with wool in multilayers essentially through hydrogen bonding of the OH.....O type. No single law can explain the complete isotherm from zero to saturated vapour pressure at any temperature.

ii) Reduction in sorption by dyed wool suggests blocking of the pores of the fibre by discrete dye crystallites.

iii) Similar reduction may also take place on account of the presence of firmly bound molecules, e.g. isopropyl alcohol or benzene present in the dry states.

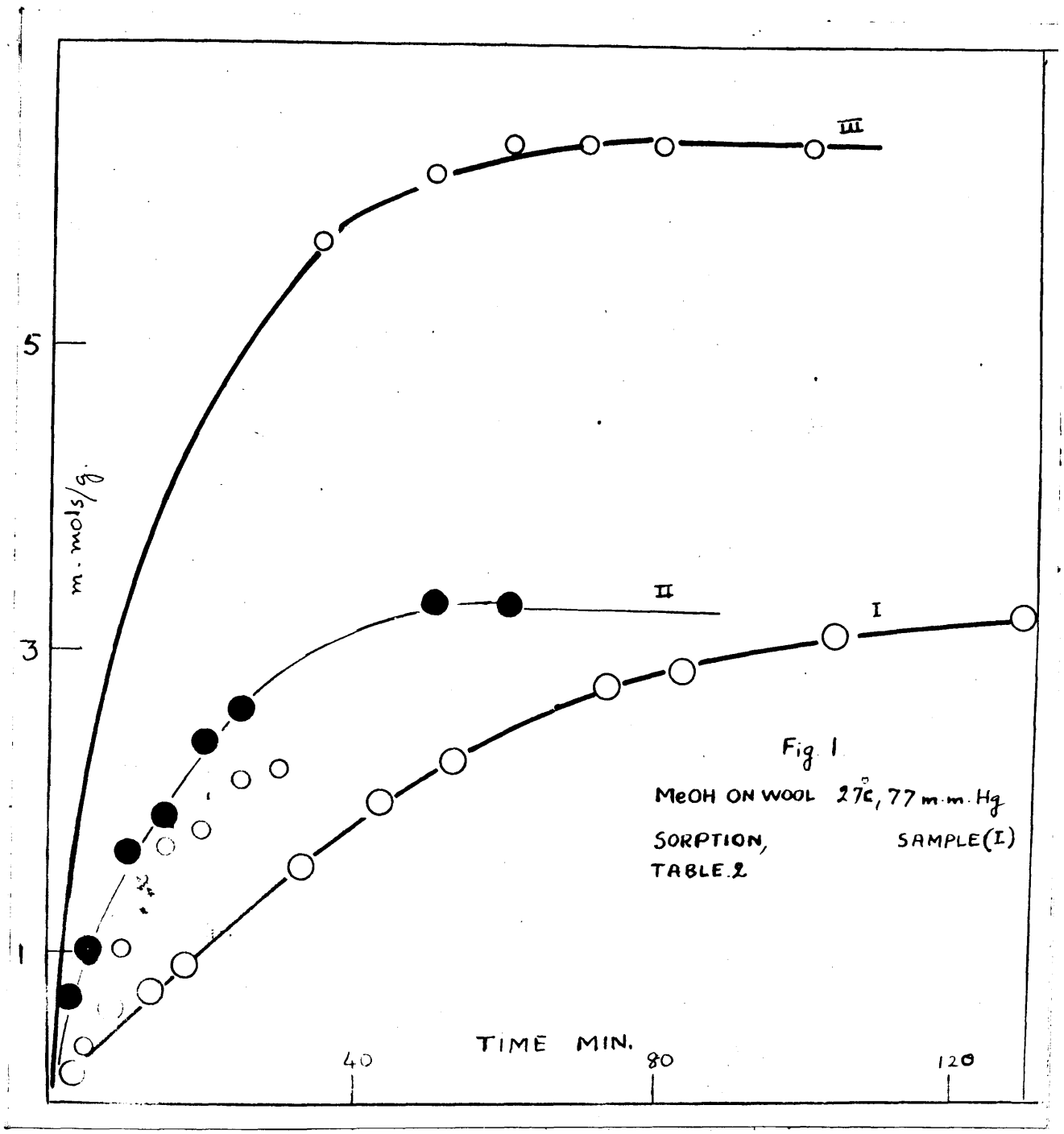

Fig 1

MeOH ON WOOL 27°C, 77 m.m. Hg

SORPTION, SAMPLE (I)

TABLE 2

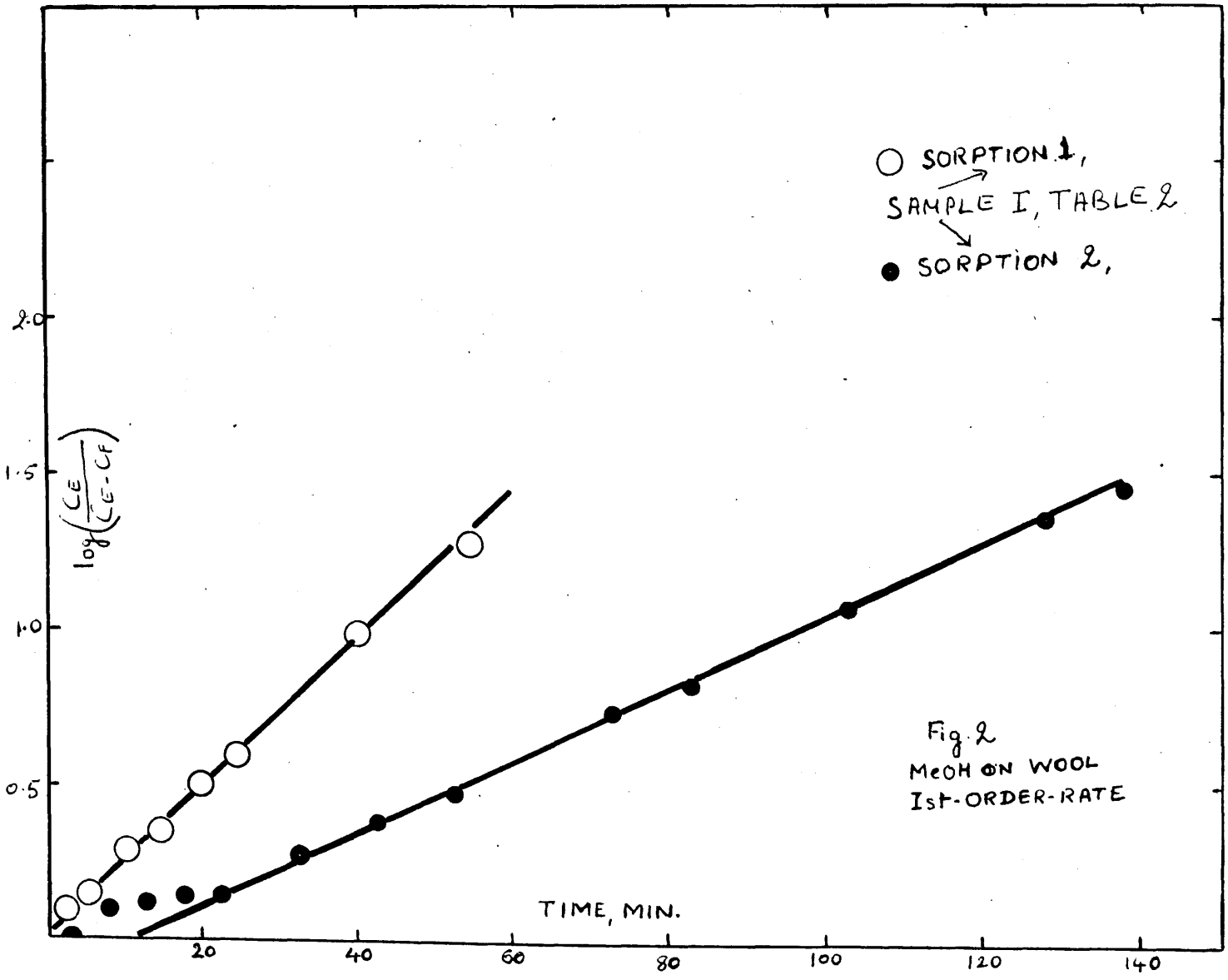

Fig. 2
MeOH ON WOOL
1st-ORDER-RATE

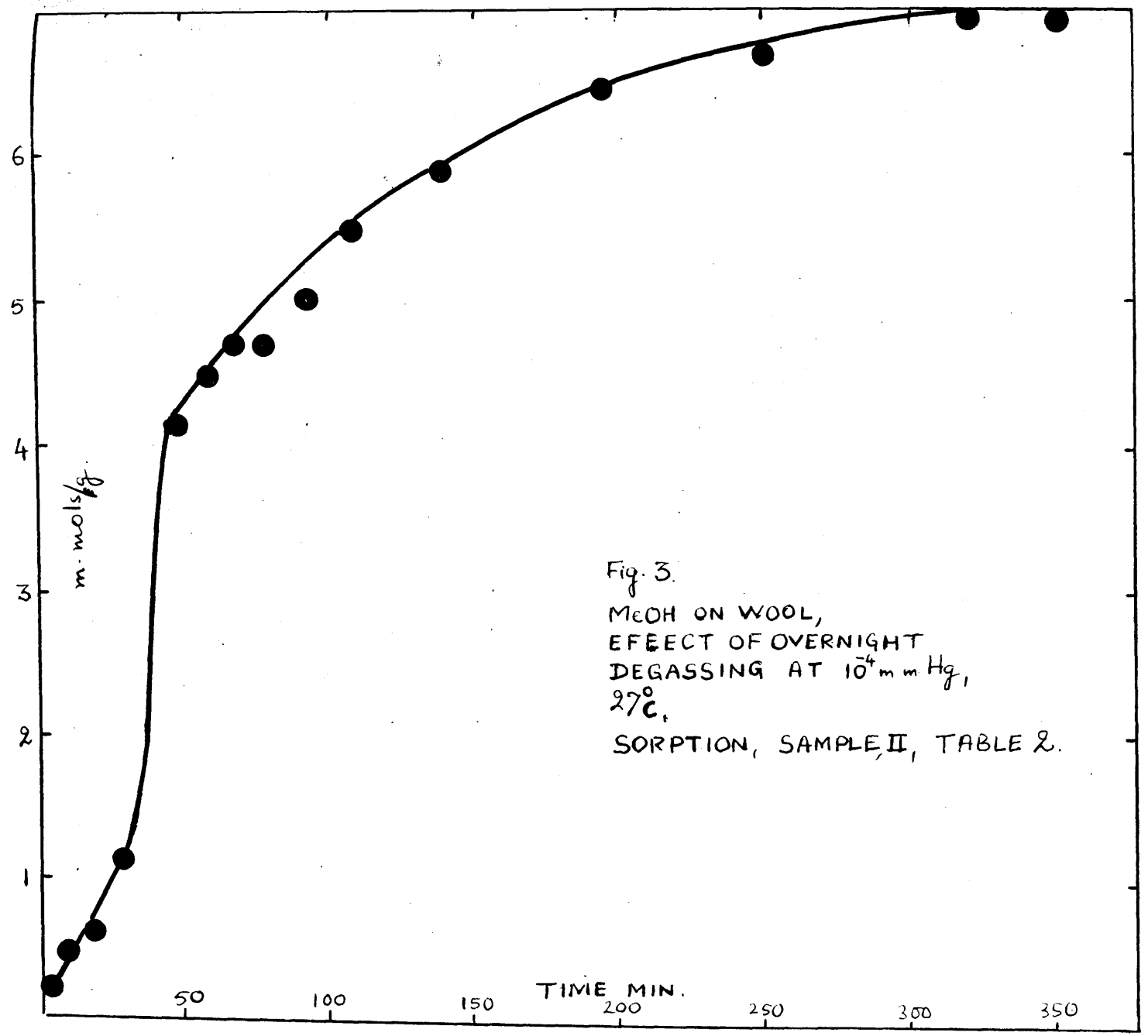

Fig. 3.
MeOH ON WOOL,
EFFECT OF OVERNIGHT
DEGASSING AT 10^{-4} m m Hg,
27°C.
SORPTION, SAMPLE II, TABLE 2.

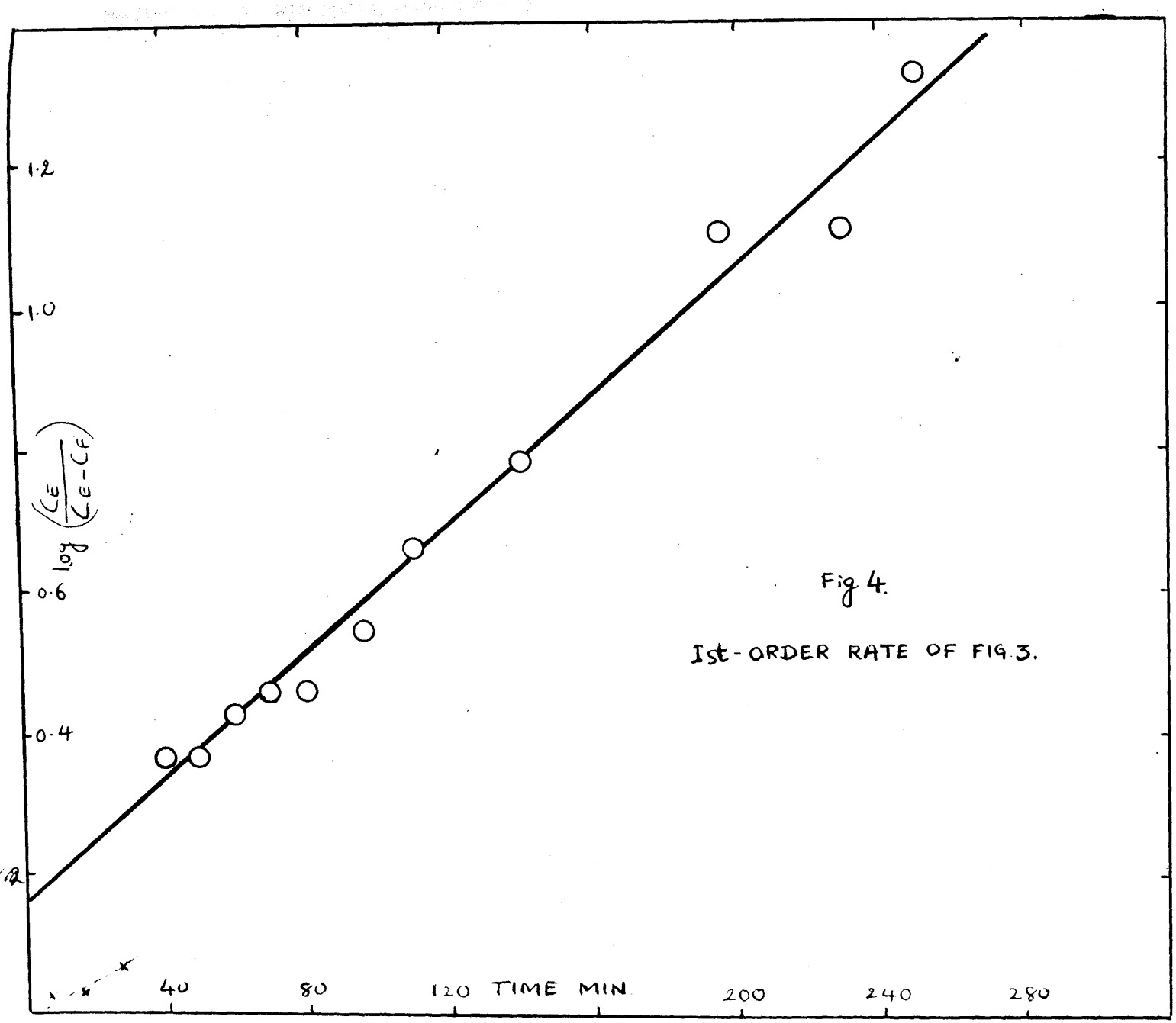

Fig 4.

Ist-ORDER RATE OF FIG. 3.

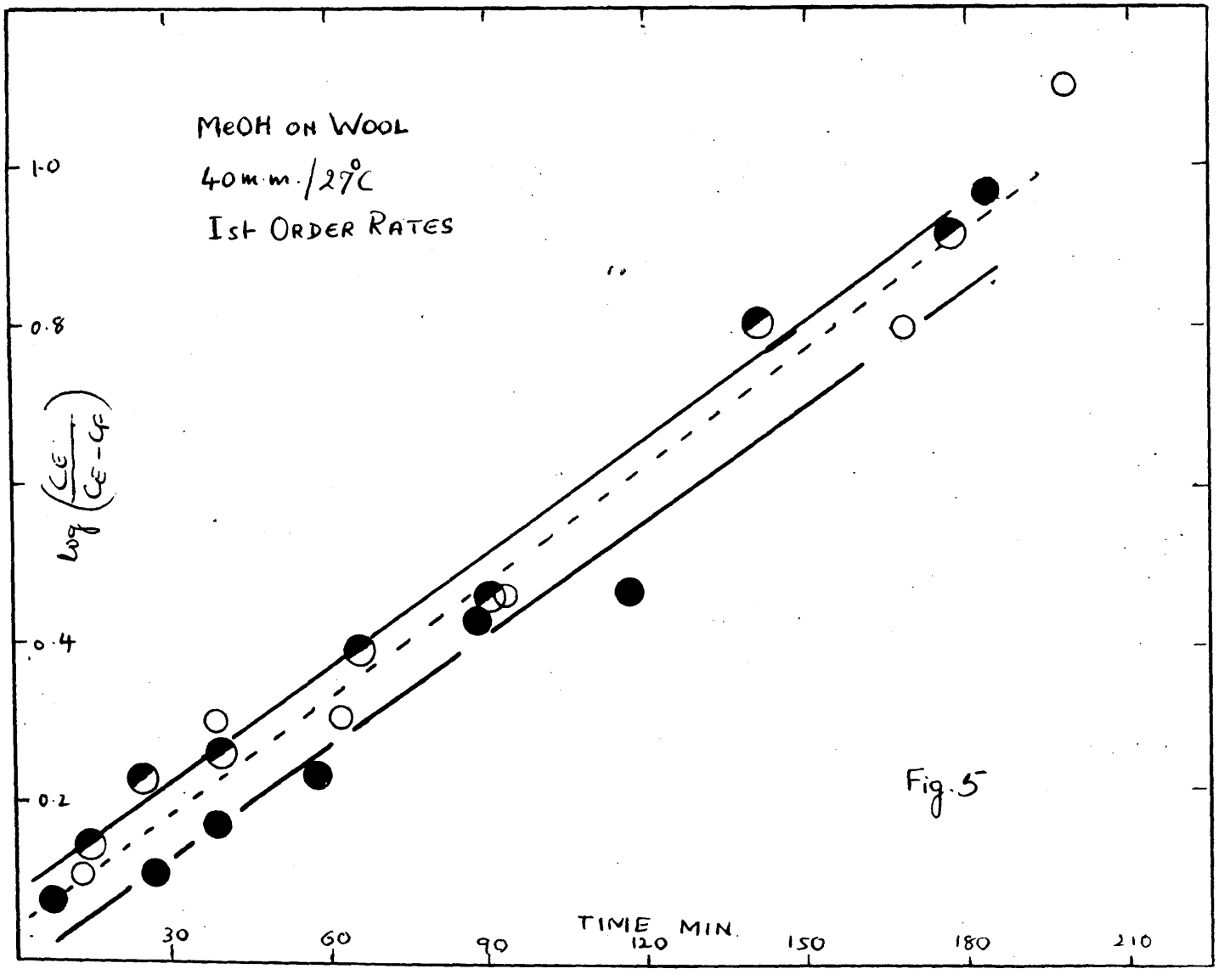
MeOH on Wool
40 m.m./27°C
Ist Order Rates
1·0
0·8
0·4
0·2
$\log\left(\frac{C_E}{C_E - C_F}\right)$
30
60
90
120
150
180
210
TIME MIN.

Fig. 5

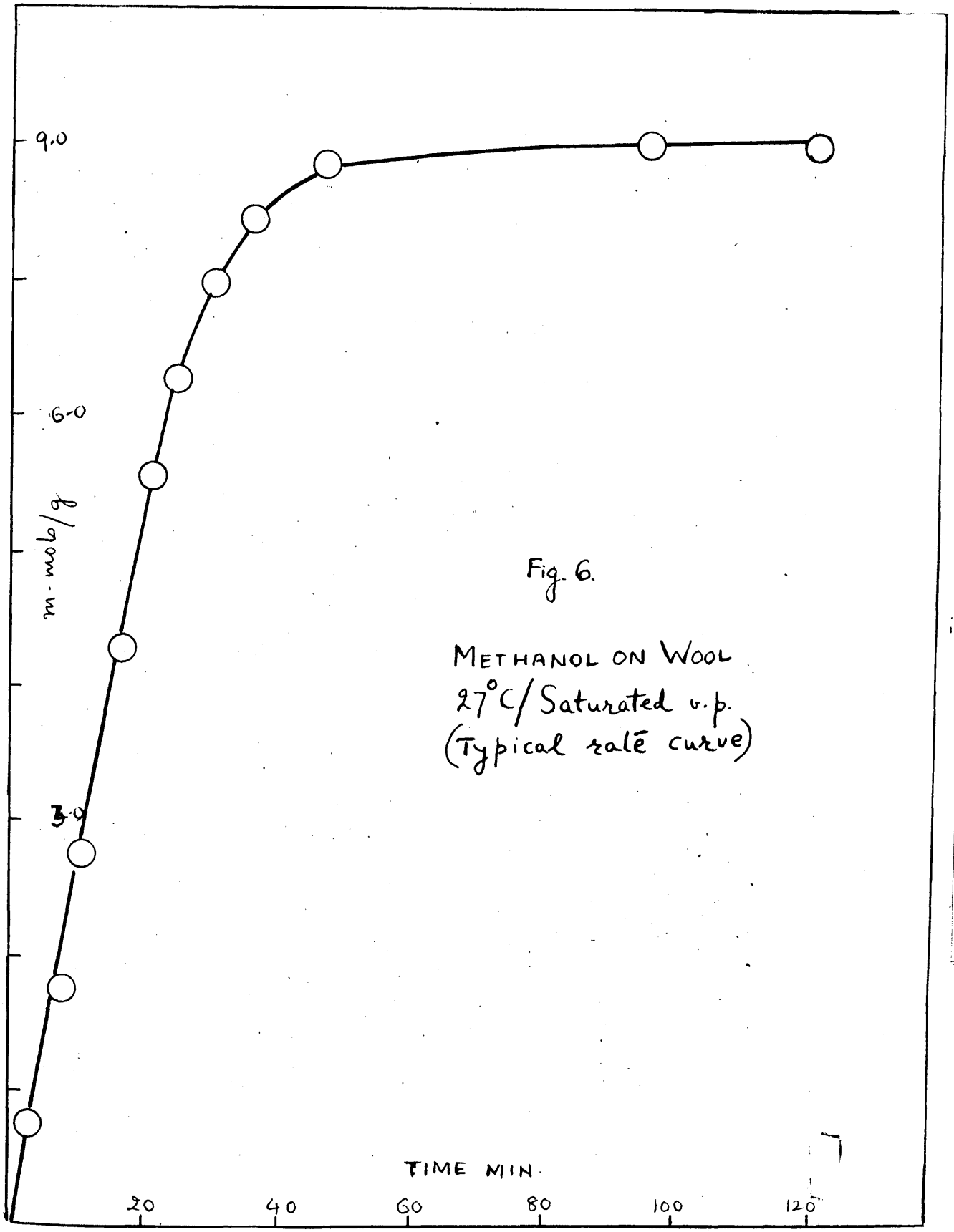

Fig. 6.

METHANOL ON WOOL
27°C / Saturated v.p.
(Typical sale curve)

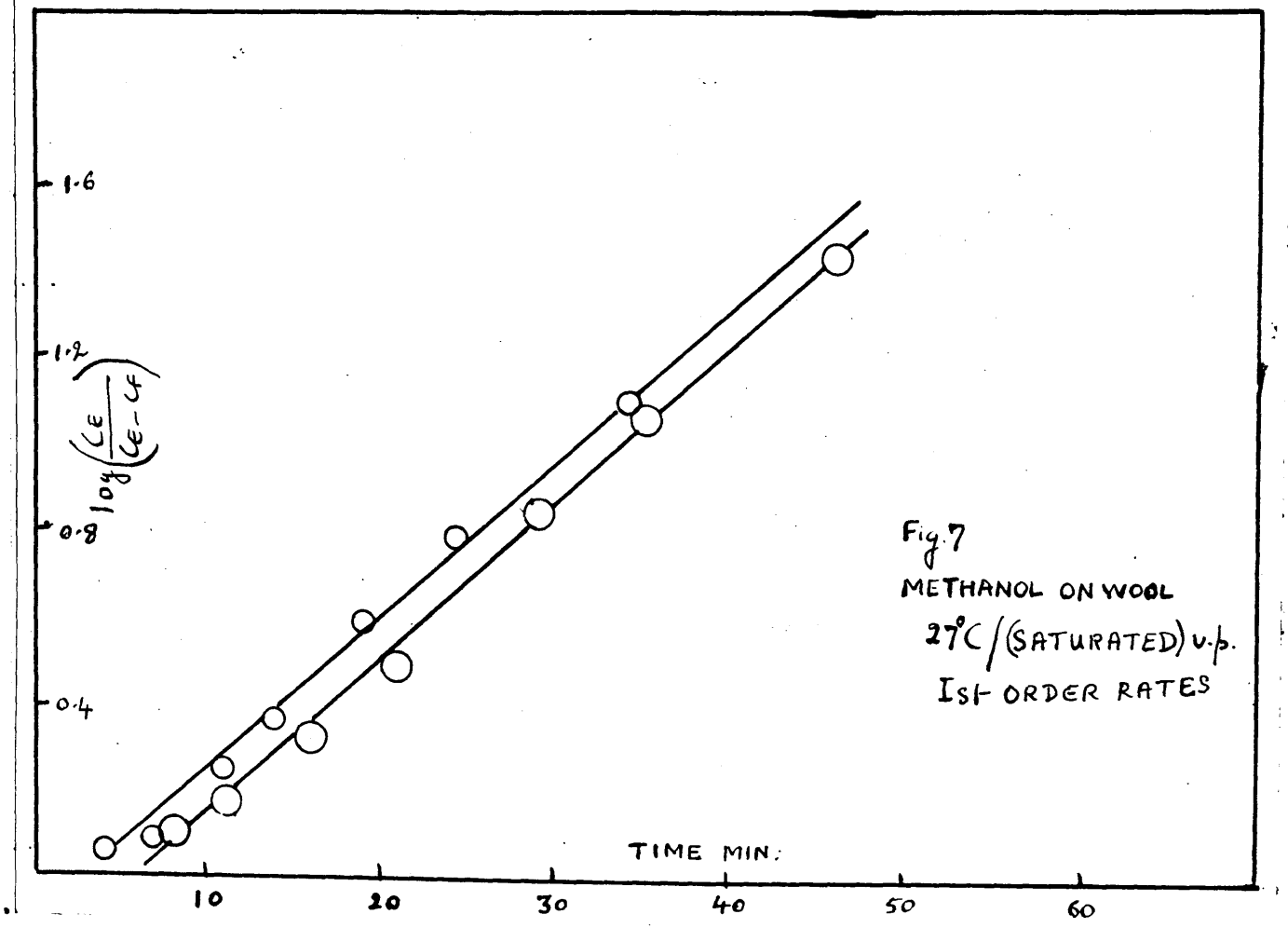

Fig. 7
METHANOL ON WOOL
27°C / (SATURATED) v.p.
1st ORDER RATES

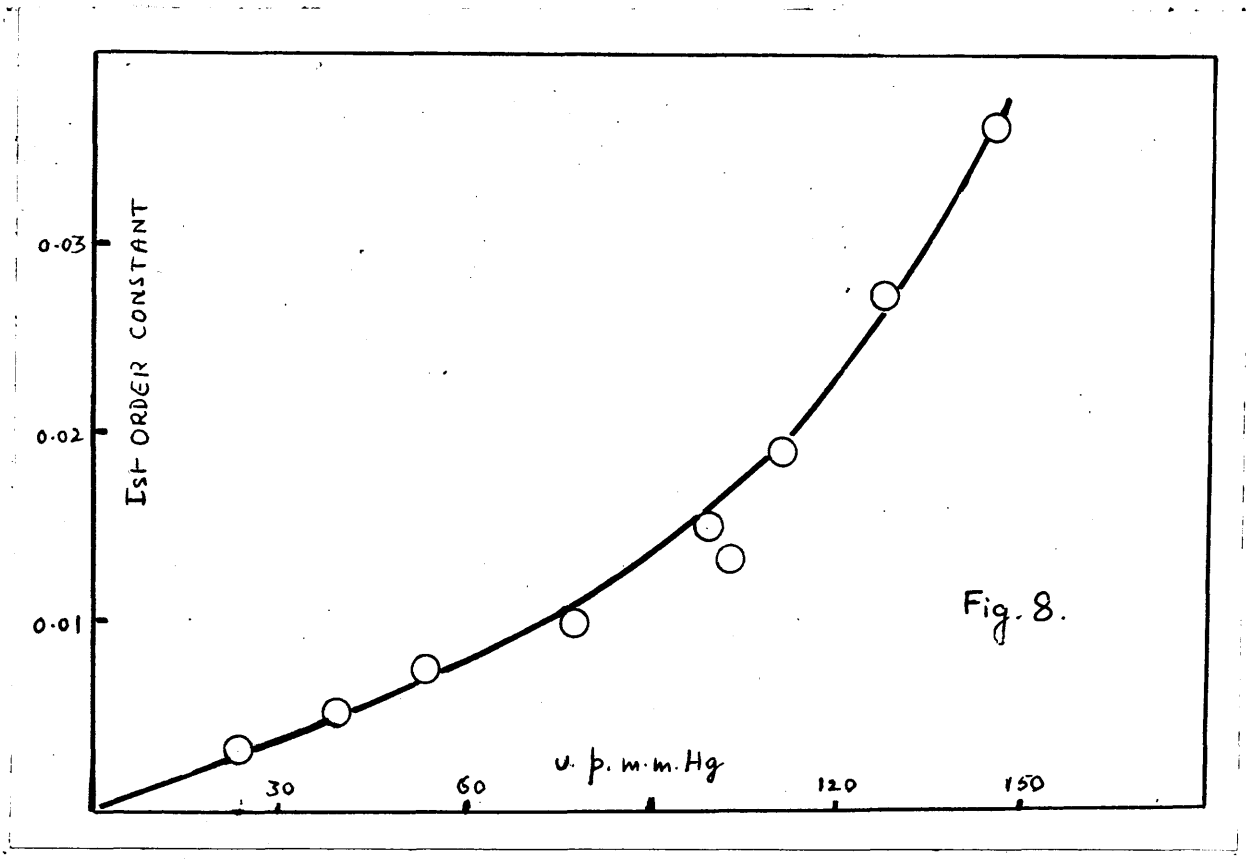

Fig. 8.

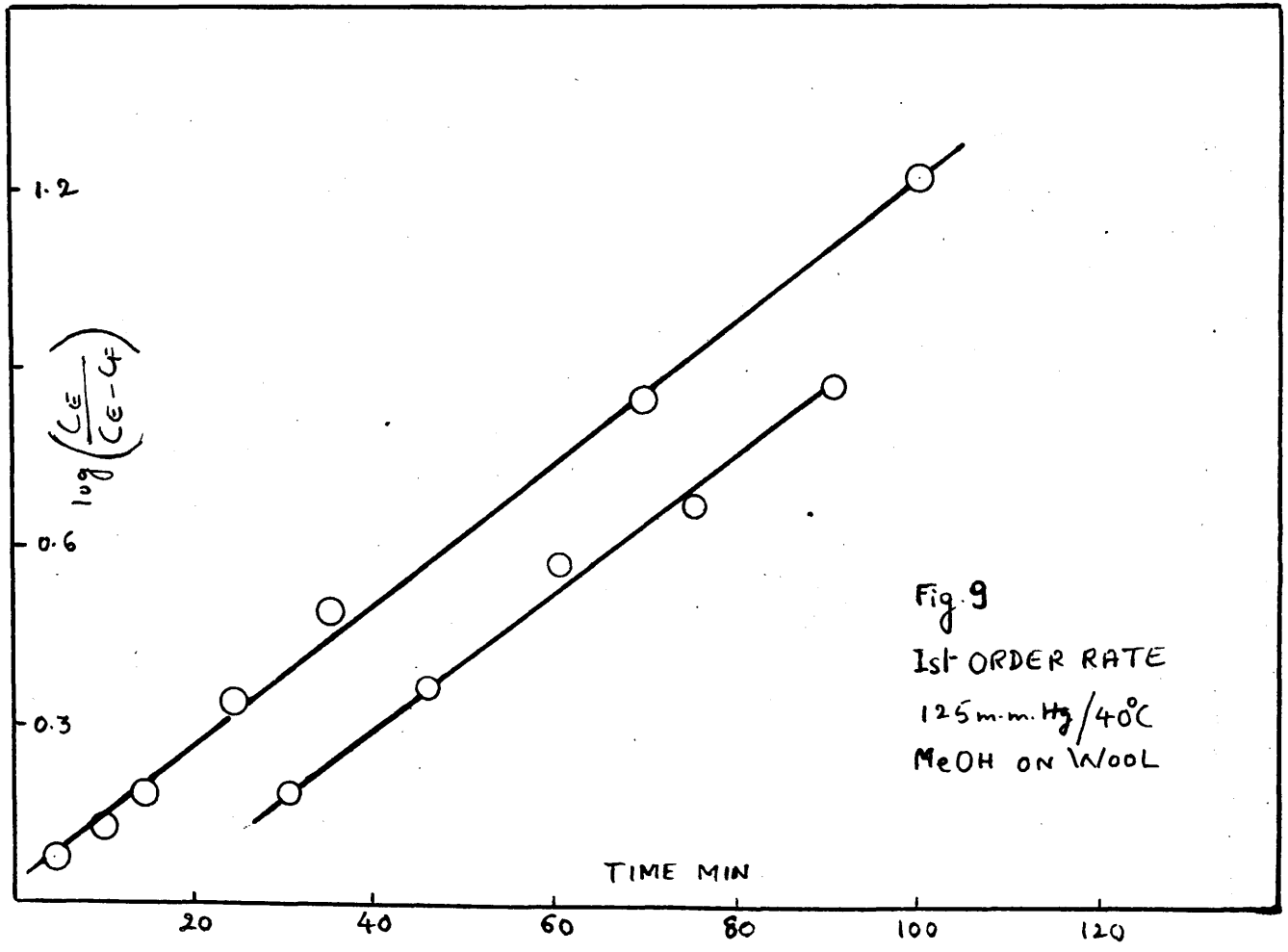

Fig. 9
Ist ORDER RATE
125 m.m. Hg / 40°C
MeOH ON WOOL

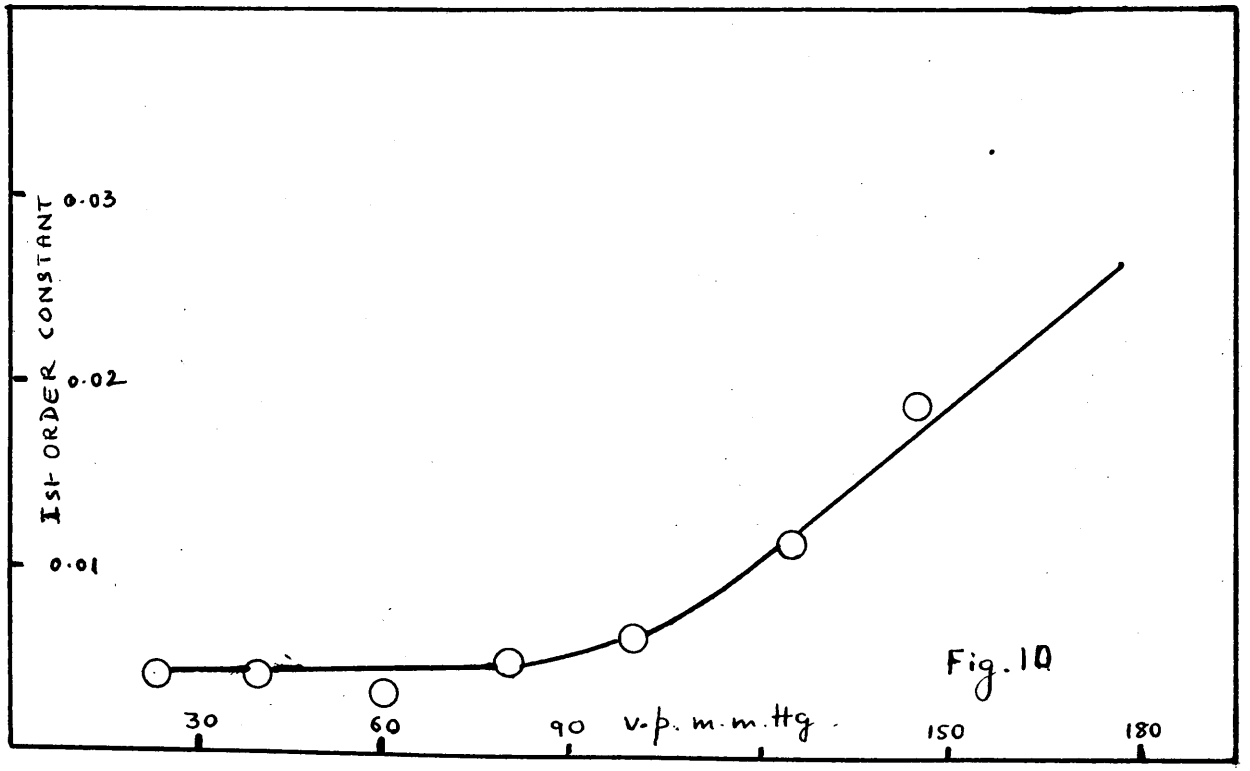

Fig. 10

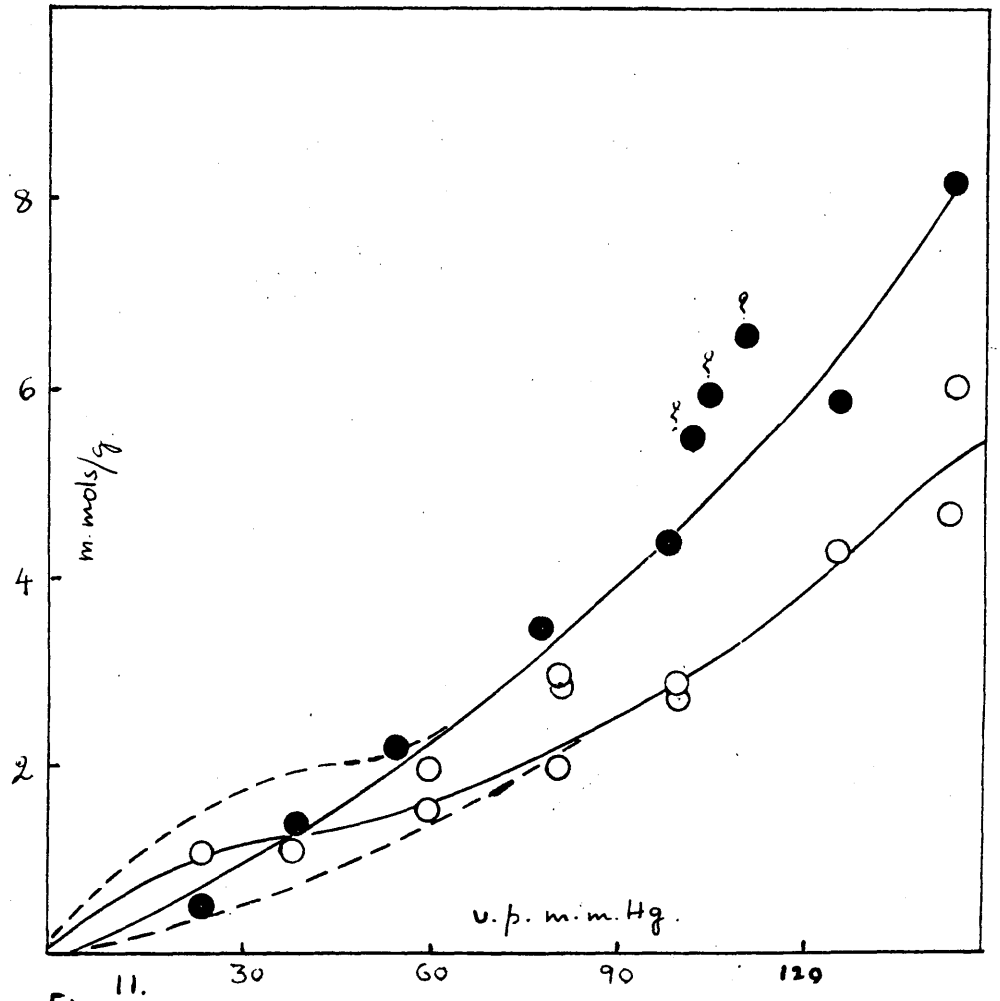

Fig 11. ORDINARY ISOTHERMS OF METHANOL ON WOOL
27°C and 40°C

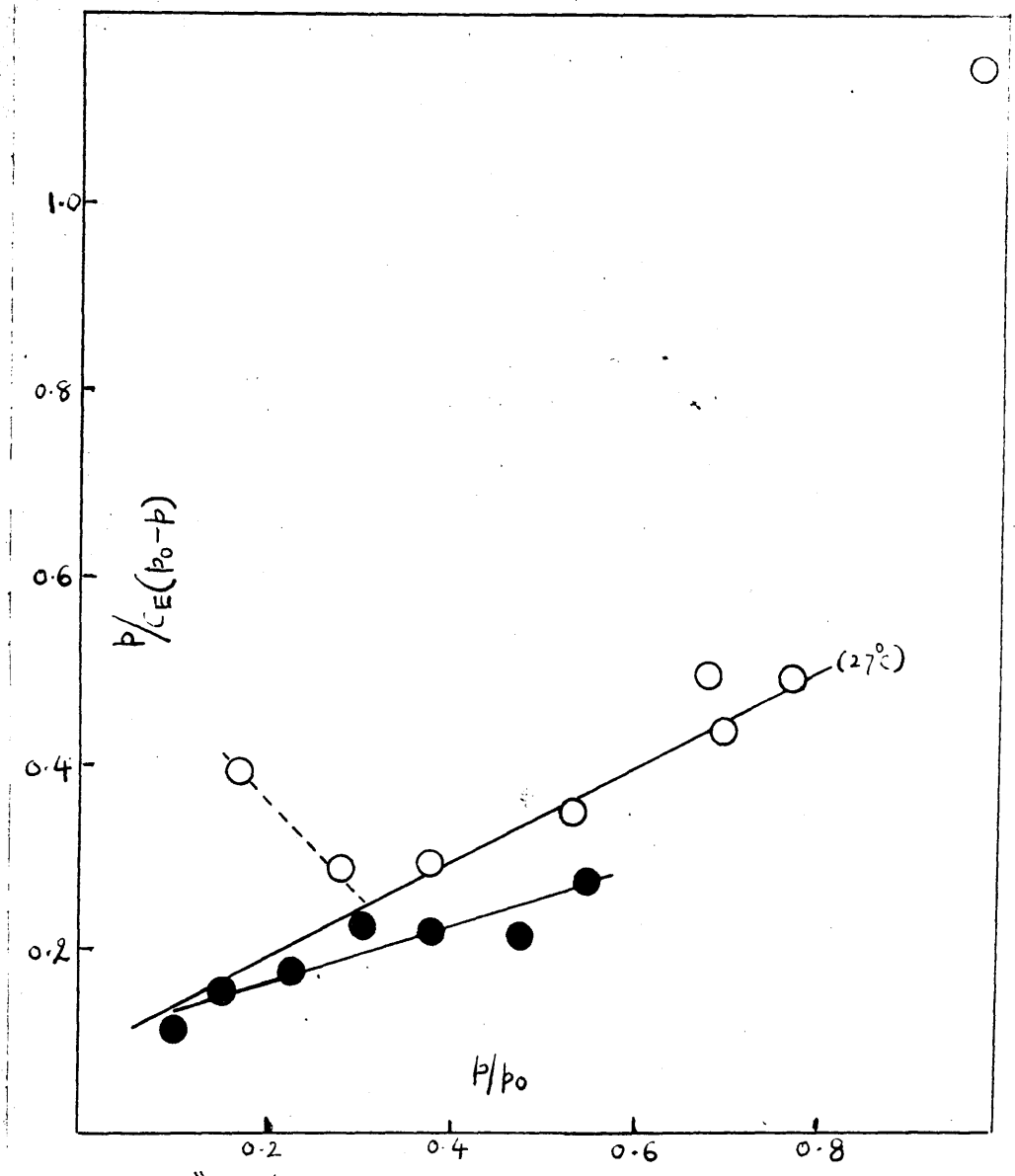

Fig 12. "BET" DATA APPLIED TO ISOTHERMS AT 27°C and 40°C

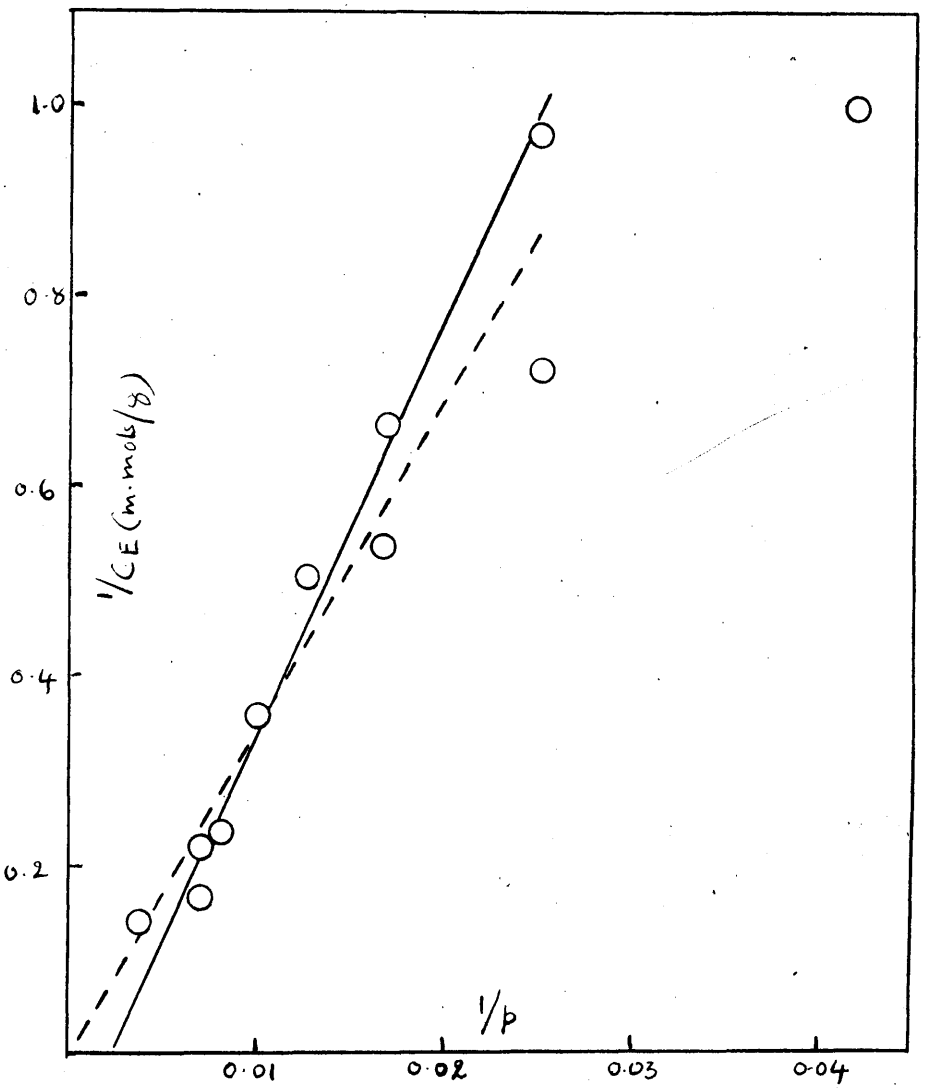

Fig. 13. Langmuir Data to Isotherm at 40°C
Methanol on Wool

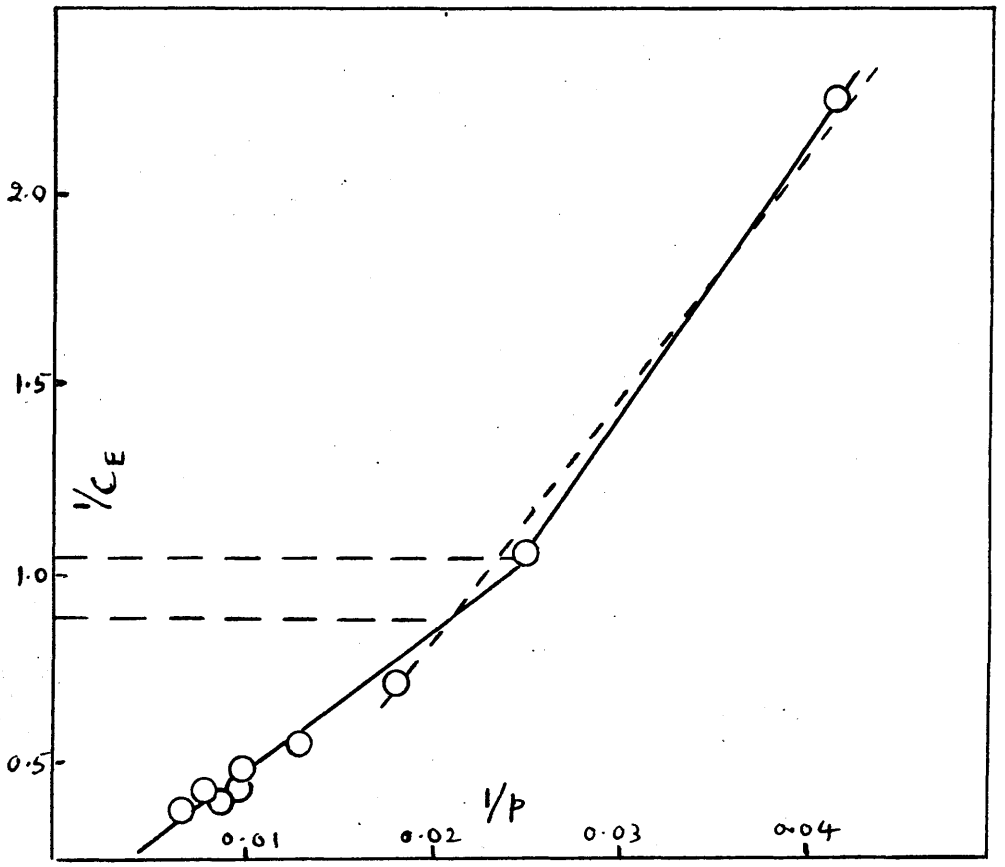

Fig. 14. Langmuir Data applied to Isotherm at -27°C
Methanol on Wool.

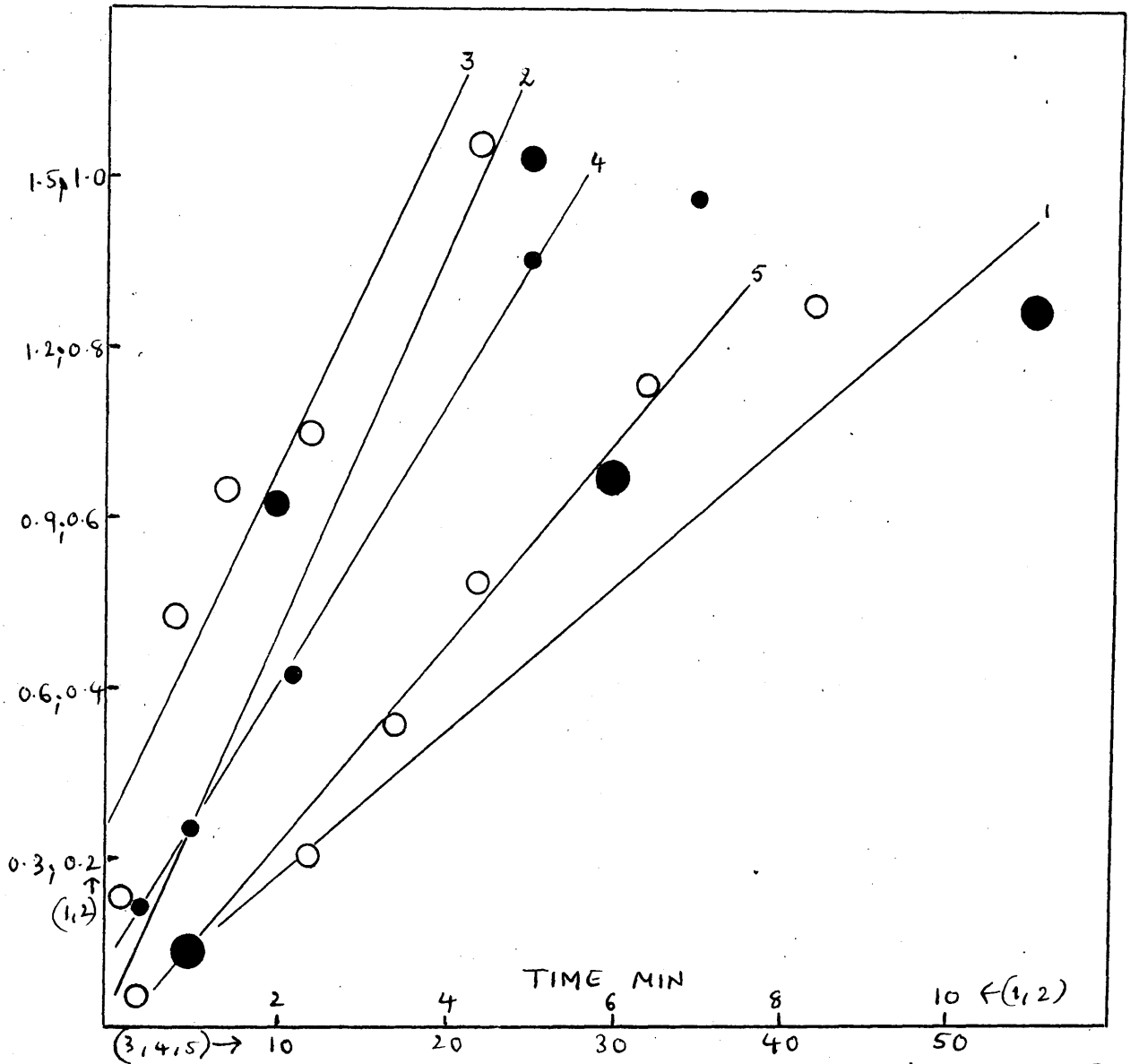

Fig.15. (IST ORDER) RATES OF SORPTION ON VARIOUSLY DRIED WOOL AT 40°C (METHANOL ON WOOL)

1. Ether
2. Isopropyl alcohol
3. Benzene
4. Acetic anhydride
5. Methanol.

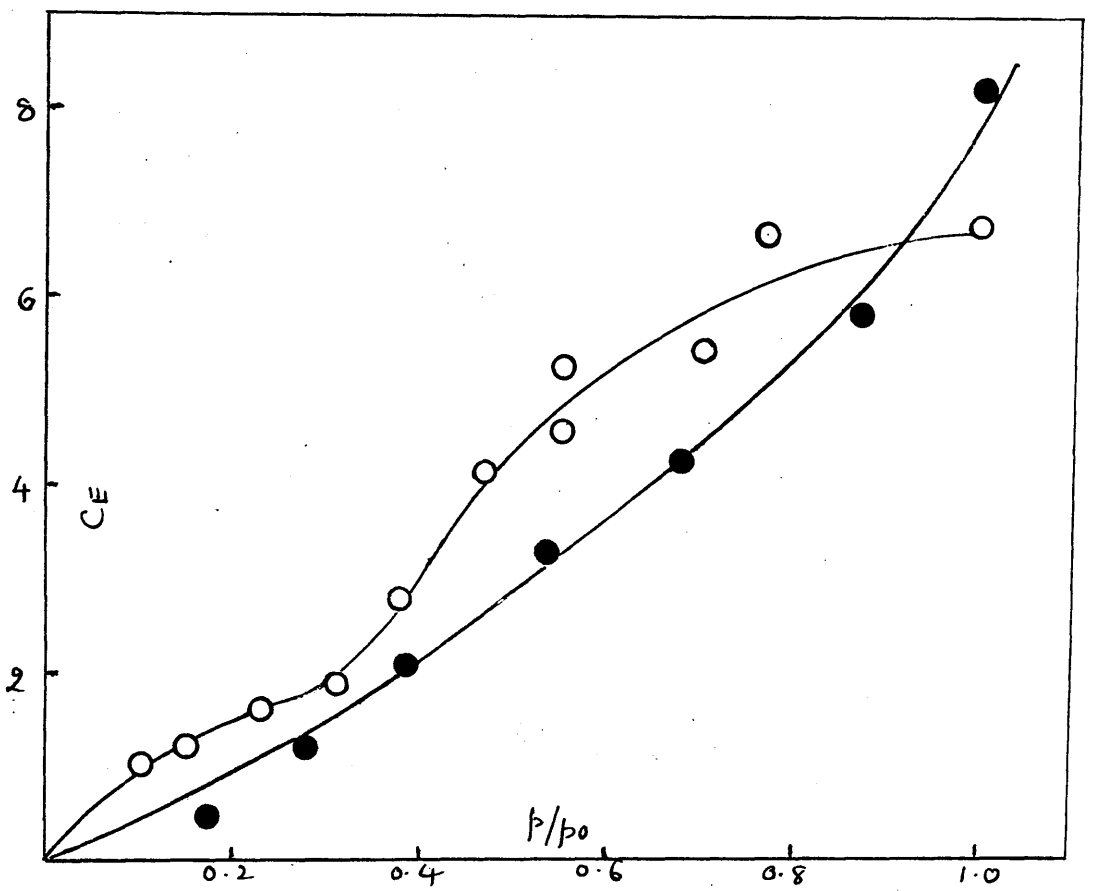

Fig. 16 C_F (m.mols/g) vs Relative vap. (p/po)

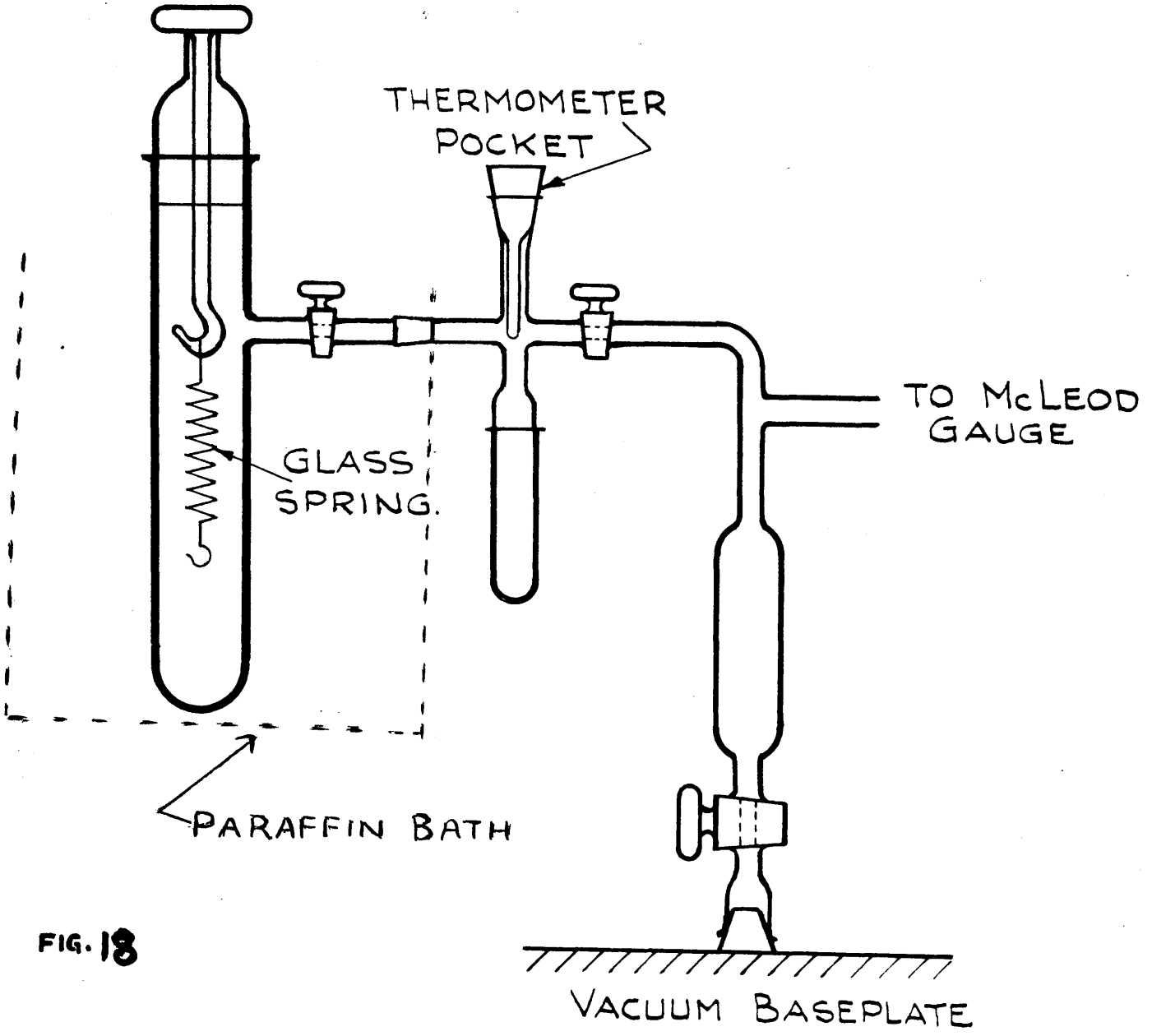
THERMOMETER
POCKET
TO McLEOD
GAUGE
GLASS
SPRING.
PARAFFIN BATH
VACUUM BASEPLATE

FIG. 18

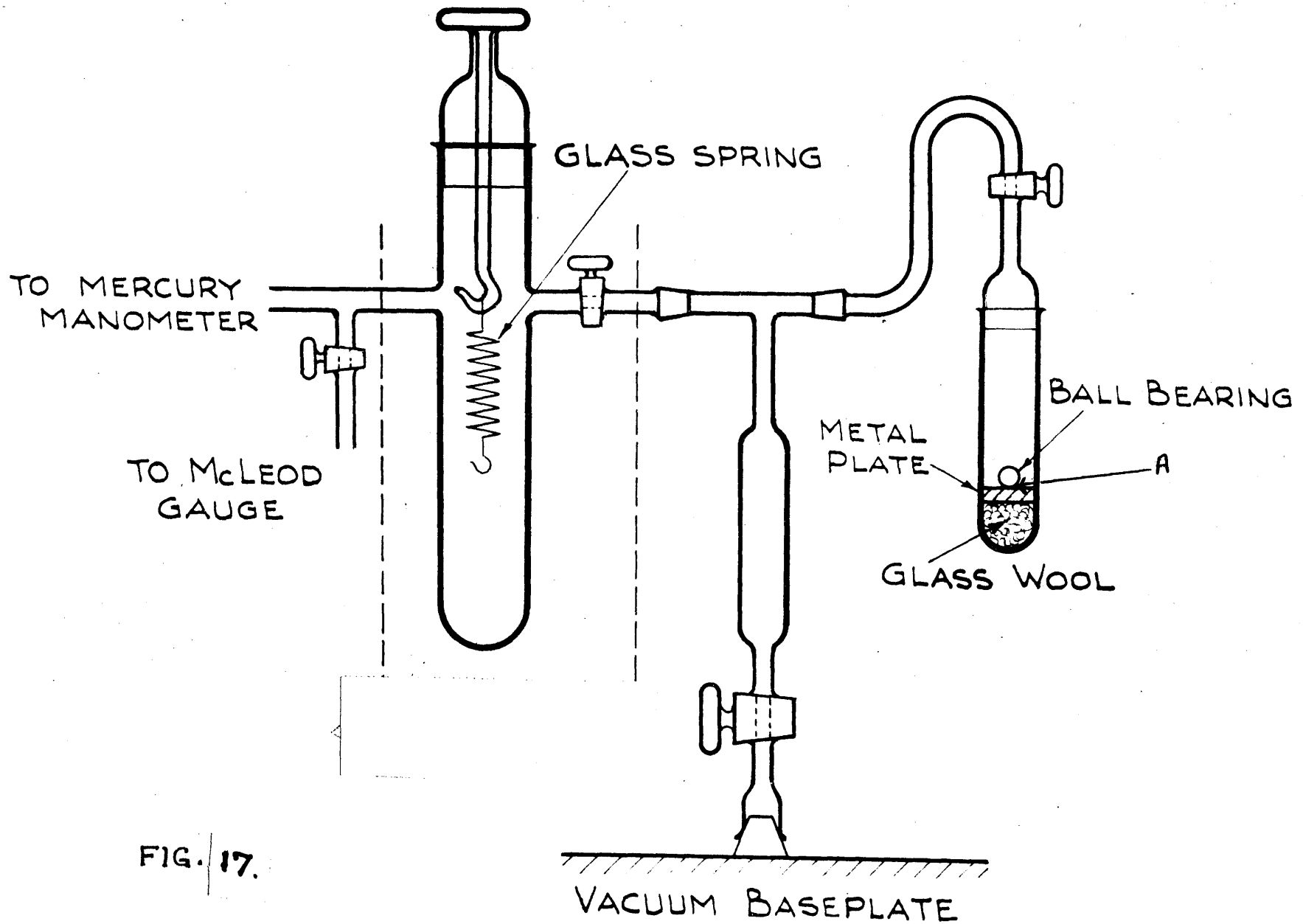
GLASS SPRING
TO MERCURY MANOMETER
TO McLEOD GAUGE
BALL BEARING
METAL PLATE
A
GLASS WOOL
VACUUM BASEPLATE

FIG. 17.

TABLE 1.

Sorption-Desorption Experiments of Dry Methanol vapour on Nylon

Sorption/ Desorption	v.p./degassing at m.m. of Hg	Temp. °C	Slope of first order curve	C_E m.mols/gm sorbed/ desorbed	Time in min
1. Sorption	76	27	0.01006	0.8874	90
Desorption	10^{-4}	"	-----	0.8874 i.e.all desorbed.	over-night
2. Sorption	76	"	0.01193	1.021	100
Desorption	10^{-4}	"	------	0.8922 i.e. 0.1288 retained	70
3. Sorption	76	"	------	1.073	100
Desorption	10^{-4}	"	------	0.7447 i.e. 0.3283 retained.	70

TABLE 2.

Sorption-Desorption Experiments on Wool

	Sorption/ Desorption	v.p./degassing at m.m. of Hg	Temp. °C	Slope of first order curve	C_E m.mols/g. sorbed/ desorbed	Time in min.
	Sample No.I.					
1.	Sorption	77	27	0.0115 ✱	3.36	180
	Desorption	10^{-4}	"	----	1.86 1.5 retained	240-300
2.	Sorption	77	"	0.0237	3.314	50
	Desorption	10^{-4}	"	----	2.620	120
	"	"	"	----	3.314 + 1.5 i.e.complete desorption	over-night
3.	Sorption	77	"	see foot-note ✱✱	6.337	60
	"	10^{-4}	"	----	2.655	120
	Sample No.II.					
1.	Sorption (after overnight degassing at 10^{-4} m.m. of Hg.	77	"	see foot-note (0.004516) §	7.0	500
	Desorption	10^{-4}	"	----	2.307 7.0 ie.incomplete desorption	175 240-300
2.	Sorption	77	"	0.0108	3.48	210
	Desorption	10^{-4}	"	----	3.13 0.35 m.mols retained	240-300
					(2.95)	140

✱ Also to be noted is that the initial points (up to 1.0 m.mols/g.) which do not fall on the straight line of the Ist order rate in the Ist cycle do so in the subsequent one. This was not so evident in nylon (possible epicuticle effect).

✱✱ There is a sudden rise in the sorption rate after 30/35 min. from 2.2 m.mols/g. to 5.6 m.mols/g. (see Fig.)

§ Sudden jump in sorption after about 30 min. from 1 m.mol/g. to about 4 m.mol/g. The Langmuir rate curve (i.e. Ist order law curve) is not obeyed for the first part of sorption while the rest of the points give the above quoted slope.

TABLE 2 (Contd.)

Sorption-Desorption Experiments of Dry Methanol Vapour on Wool

	Sorption/ Desorption	v.p./degassing at m.m. of Hg	Temp. ^{o}C	Slope of first order rate curve	C_E m.mols/g. sorbed/ desorbed	Time in min.
	Sample III					
1.	Sorption	103	27		5.264	40
	Desorption	10^{-4}	"		ca. 3.264 2.000 retained	90
	"	"	"		ca 4.514 ie 0.75 retained	240-300
2.	Sorption	103	"		4.885	151
3.	Sorption§§	103	"		5.094	105
	Desorption	10^{-4}	"		4.514 0.58 retained	overnight
4.	Sorption	103	"		4.320	74
	Desorption	10^{-4}	"		Incomplete desorption	240-300
5.	Sorption	120	"		6.362	145
	Desorption	10^{-4}	"		Incomplete desorption (1.0 retained)	240-300
6.	Sorption	120	"		5.7	100
	Desorption	10^{-4}	"		Incomplete desorption	240-300
7.	Sorption§§	120	"		3.9	165
	Desorption					

§§ was left at atmospheric pressure for 3/4 days to restore to its normal state from any stresses imposed during the sorption-desorption cycles noted above.

TABLE 3

Sorption Experiments of Dry Methanol on Dyed Wool

Sorption	v.p. m.m. of Hg	Temp. °C	Slope of first order rate curve	C_E m.mols/gm.	Time min.
Dyed with Solway Blue BNS					
Sample I	77	27	0.00833	4.0	240
Sample II	"	"		1.942	145
Sample III	"	"		1.495	135
Sample IV	"	"		2.662	855
Wool containing 1.92 m.mols/g.of Phenol(from aqueous sorption)					
Sample I	77	27	0.0163	3.3780	82
Sample II	"	"	0.008185	2.661	106
Wool containing 0.42 m.mols/g. of Phenol(from aqueous sorption)					
Sample I	77	27		3.941	165
Dyed with Coomassie Navy Blue GS.					
Sample I	78	27	0.012	2.199§§	140
Sample II	"	"	0.00905	3.302	140
Sample III	"	"	0.00905	3.234	180
Deaminated wool					
Sample I	78	27		3.459	
Dyed with Azo Geranine 2GS					
Sample I	Saturated	40		7.131	62

§§ Heavily dyed sample from the lot

Table 4.

Sorption isotherm of Dry Methanol on Wool at 27°C.

Sorption Sample No	v.p. m.m. of Hg	C_E m.mols/gm	Slope of first order rate curve	Time min.
1	24	0.4420		145
2	"	0.5041 (0.52)*	(0.003031)*	180 (250)*
3	40	(1.35) 1.14	(0.005238)	(280) 200
4	"	(1.38) 1.23	"	(280) 181
5	"	(1.38) 1.313	"	(280) 200
6	55	1.9410	0.0075	(300) 220
7	"	2.372	0.00733	(300) 240
8	77	(4.31)	(0.009 or 0.01)	(180)
9	98	4.325	0.015	180
10	101	5.455	0.0134 ?	112
11	105	5.943	0.0275 ?	50
12	110	6.754	0.019	110
13	125	5.845	0.0275 (0.023)	60 (33)
14	Saturated (145)	8.0370 (8.2)	(0.036)	(94)
15	"	8.502	"	(74)
Refer 16	77	3.36	0.0115	180
Table 17	77	3.314		120
2 18	77	3.48	0.0108	210

* Extrapolated value

TABLE 5.

Sorption-isotherm of Dry Methanol on Wool at 40°C.

Sorption Sample No	v.p. m.m.of Hg	C_E m.mols/gm	Slope of first order rate curve	Time min.
1	24	1.0140	0.004169	280
2	40	1.030	0.004169	135
3	"	1.387	---	250
4	60	1.882	0.003215	285
5	"	1.5140	"	256
6	80	2.932 ?	0.004737	205
7	"	2.872 ?	0.008751	194
8	"	1.969	0.004167	175
9	100	2.785	0.00625	316
10	"	2.845	"	145
11	125	4.239	0.01123	130
12	125	4.166	"	151
13	145	4.643	0.0188	103
14	145	6.055	"	75
15	Saturated (260.5)	6.539	0.046	32
16	"	7.106	0.045	77

TABLE

Heats of Sorption

Clausius Clapeyron Equation: 5133, 4179, 4375 cals/mol.

TABLE 6

Sorption-Desorption Experiments on Specially Dried Wool at 40°C.

Sample No.	Sorption/ Desorption	v.p./ degassed at m.m. of Hg	C_E m.mols/gm Sorbed/ Desorbed	Slope of Ist. order rate curve	Time min	Drying method Final soaking agent
1.	Sorption	Saturated	5.2740	0.08571	26	Ether (dry)
	Desorption	10^{-4}	4.559		90	"
			5.2740		195	"
2.	Sorption	Saturated	5.182	---	37	Benzene (dry)
3.	Sorption	Saturated	4.360	0.221	10	Isopropyl alcohol
4.	Sorption	Saturated	6.0120	0.030	57	Methanol (dry)
	Desorption	10^{-4}	5.238		64	"
			6.0120		209	"

TABLE 7

Miscellaneous Vapours on Wool at Saturated v.p.

Compound	Temp. °C	v.p. m.m. of Hg	C_E m.mols/g	Time min.
Pyridine*	40	37	nil	overnight
Benzene (dry)	"	185	0.062	400
n-Propyl-alcohol	"	28	0.028	overnight
Dioxan	27	44	0.5093	110

* dried over NaOH and redistilled

TABLE 8

Sorption rate of dry Methanol on Wool

Temp. 27°C. v.p. 24 m.m.Hg.		Temp. 27°C.		v.p. 55 m.m. Hg.	
Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.
20	0.1260	4	0.3376	10	0.2702
55	0.2770	14	0.4220	20	0.4504
90	0.4285	24	0.7314	35	0.7506
135	0.5041	49	0.9847	55	0.9007
165	0.5041	69	1.1530	85	1.3510
190	0.5041	109	1.4630	115	1.6510
Extrapolated C_F value (for		144	1.8010	145	1.8920
equilibrium sorption)		184	1.9410	190	2.312
= 5.2 from the nature of		219	1.9410	235	2.312
the curve		Extrapolated C_E = 2.0		Extrapolated C_F = 2.45	

TABLE 9

Temperature 27°C. v.p. 77 m.m. of Hg.

Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.
5	0.1528	45	2.215
10	0.8555	80	3.33
15	1.10	115	3.925
20	1.283	145	4.307
25	1.375	175	4.307
35	2.215		

TABLE 10

Temp. 27°C	v.p. 98 m.m. of Hg	Temp. 27°C	v.p. 101 m.m.of Hg	Temp. 27°C	v.p. 105 m.m.ofHg.
Time min.	m.mols/g.	Time min.	m.mols/g.	Time min.	m.mols/g
4	0.4804	7	0.6624	2	0.3984
11	1.1240	12	1.8310	5	1.4610
16	1.7320	17	2.3380	11	2.9540
21	2.1570	20	2.7670	20	3.9170
31	2.8560	32	3.3120	26	4.9140
46	3.4620	40	3.9750	35	5.3780
56	3.888	52	4.4810	50	5.9430
96	4.250	62	5.0650	75	"
126	(4.250)	72	5.2220	95	"
156	(4.350)	92	5.2990	110	"
186	4.350	112	5.4550		
		142	5.4550		
		172	5.4550		

TABLE 11

Temp. 27°C.	v.p. 110m.m.of Hg	Temp. 27°C.	v.p. 125 m.m.of Hg	Temp	v. p.
Time min.	m.mols/g.	Time min.	m.mols/g.	Time min.	m.mols/g.
3	0.6395	2	0.4055		
7	1.7590	6	1.3520		
13	2.6780	8	----		
19	3.3170	11	2.4670		
30	4.5560	21	4.3580		
40	5.3950	26	5.2040		
50	5.8750	33	(6.049)		
60	6.3160	46	(6.2520)		
80	6.6740	51	(6.1840)		
110	6.7540	63	5.845		
140	6.7540	81	"		
		106	"		

C_E = 5.845

TABLE 12

Temp. 40°C	v.p. 145 m.m.of Hg	Temp. 40°C	v.p. 145m.m.of Hg	Temp. 40°C	v.p. 145 m.m.ofHg
Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.
5	0.9432	5	1.714	2	0.6697
13	1.306	10	2.856	7	2.997
18	1.850	15	3.599	13	4.943
23	2.213	25	4.057	17	5.964
33	3.083	45	5.714	32	6.539
43	3.700	75	6.055	57	"
53	4.316	105	"	67	"
73	4.571	135	"	87	"
103	4.643			117	"
133	"				

TABLE 13

Temperature 40°C. v.p. Saturated (260.5)

Time min.	Sorption m.mols/g.	Time min	Sorption m.mols/g	Time min.	Sorption m.mols/g
2	0.8612	22	6.424	77	7.106
7	2.834	27	6.531	117	7.106
12	4.624	62	6.819		

TABLE 14.

Temp. 40°C.	v.p. 100 m.m.of Hg	Temp. 40°C.	v.p. 125 m.m.of Hg	Temp. 40°C.	v.p. 125 m.m.ofHg
Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.
8	0.3402	5	0.6468	5	0.4968
16	0.5816	10	1.0420	10	0.6017
16	1.2400	15	1.4730	18	---
36	1.5250	25	2.3170	31	1.4960
56	"	35	2.8740	46	2.3610
86	1.7880	50	3.5920	61	3.0400
121	2.250	70	3.6280	76	3.2870
166	2.535	100	3.9870	91	3.5650
316	2.7850	130	4.2390	121½	4.0260
376	"	160	"	151	4.166
		180	"	166	"
		220	"	181	"

TABLE 15.

Temp. 40°C	v.p. 24 m.m.of Hg	Temp. 40°C.	v.p. 40 m.m.of Hg.	Temp. 40°C.	v.p. 40 m.m.of Hg.
Time mind	Sorption m.mols/g.	Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.
10	0.1778	15	0.08732	10	0.5473
40	0.3911	30	0.3667	45	0.8026
100	0.6757	45	0.4366	250	1.3870
160	0.9601	60	0.6811		
220	1.0140	90	1.030		
280	"	135	"		
		285	"		

TABLE 16

Temp. 40°C	v.p. 60m.m.ofHg	Temp. 40°C	v.p. 60 m.m.of Hg	Temp. 40°C	v.p. 80 m.m. of Hg
Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.	Time min.	Sorption m.mols/g.
5	0.1153	5	0.7015	10	0.3558
10		36	0.8307	25	0.8642
35	0.2689	66	0.8859	45	1.1020
75	0.9219	256	1.5140	65	1.4060
115	1.0760			100	1.7120
285	1.8860			125	1.8470
315	"			165	2.4910
345	"			205	2.9320

TABLE 17

Temp. 40°C	v.p. 80 m.m.of Hg	Temp. 40°C	v.p. 80 m.m.ofHg	Temp. 40°C	v.p. 100 m.m.Hg
Time min.	Sorption m.mols:g	Time min.	Sorption m.mols/g	Time min.	Sorption m.mols/g.
9	0.8861	5	0.4057	5	0.4323
19	1.1310	15	0.4508	15	0.7914
29	1.2220	25	1.0220	25	1.017
39	1.2380	85	1.1270	35	1.244
64	2.0170	115	1.3380	55	1.5450
94	2.200	145	"	85	2.1110
124	2.475	175	"	115	2.7130
164	2.750			140	2.845
194	2.872			175	"
224	"				
254	"				

TABLE 18

Sorption-Desorption Experiments of Methanol (dry) on variously dried Wool at 40°C and Saturated v.p.

Final soaking agent	Ether (dry)		
Sorption		Desorption	
Time (min)	m.mols/g	Time (min)	m.mols/g.
1	0.9419	1	2.599
6	4.1070	5	4.145
11	4.522	10	4.409
26	5.2740	30	4.559
56	"	69	"
86	"	90	"
116	"	195	5.2740

Final soaking agent	Methanol (dry)		
2	0.7387	1	2.216
12	3.123	2	3.224
17	4.164	4	3.895
22	5.037	9	4.298
32	5.575	19	4.806
42	5.709	24	"
57	6.012	64	5.238
77	"	89	5.675
87	"	119	
		169	5.842
		209	6.012

TABLE 19

Sorption Experiments of Methanol (dry) on variously dried Wool at 40°C. and Saturated v.p.

Final soaking agent Benzene (dry)		Final soaking agent Isopropyl alcohol	
Time (min)	m.mols/g.	Time (min)	m.mols/g.
1	2.165	2	3.278
4	4.223	5	3.980
7	4.613	10	4.360
12	4.721	25	"
22	5.040	40	"
37	5.182	55	"
52	"		
62	"		
92	"		
122	"		

REFERENCES

Brunauer, The Adsorption of Gases and Vapours, Oxford Univ.Press., 1944, p.150

Bull, J.A.C.S., 1944, 66, 1499.

Carlene, J.S.D.C., 1944, 60, 232.

Cassie, Trans.Faraday Soc., 1943, 41, 450, 458.

Symp. S.D.C., 1946, p. 86.

Chipalkatti V.B., Ph.D. Thesis, Glasgow University, 1950.

Dole and McLaren, J.A.C.S., 1947, 69, 651.

Gilbert, Symp. S.D.C., 1946, p. 96.

Giles and Chipalkatti, Nature, 1950, 165, 735.

Hailwood and Horrobin, Discussions of the Faraday Soc., 1948, 428, 84.

Kanmaru and Chao, Kolloid Z., 1938, 84, 85

King, Trans.Faraday Soc., 1940,36,445; ibid.1945,45,325; ibid.1947,2, 551.

Larose, J.S.D.C., 1954, 70, 77.

Lauter, Kolloid Z., 1944, 107, 86.

McBain and Bakr, J.A.C.S., 1926, 48, 690.

McLaren and Rowen, J.Polymer Sci., 1951, 7, 289.

Pierce, J.T.I., 1929, 21, T 133.

Shepperd and Newsome, J.Phys.Chem., 1929, 33, 1826.

Speakman, J.S.D.C., 1933, 44, 180.

Urquhart and Williams, J.T.I., 1924,15, T146, T138, T433; ibid.,1925, 16, T 155; ibid, 1929, 20, T.125.

§§§§§§§§§§§

APPENDIX

Part I. of this Thesis has been submitted for publication to the Journal of the Society of Dyers and Colourists and is awaiting referee's report.

The other Parts (IIA. and IIB.) are shortly being submitted to other journals for publication.